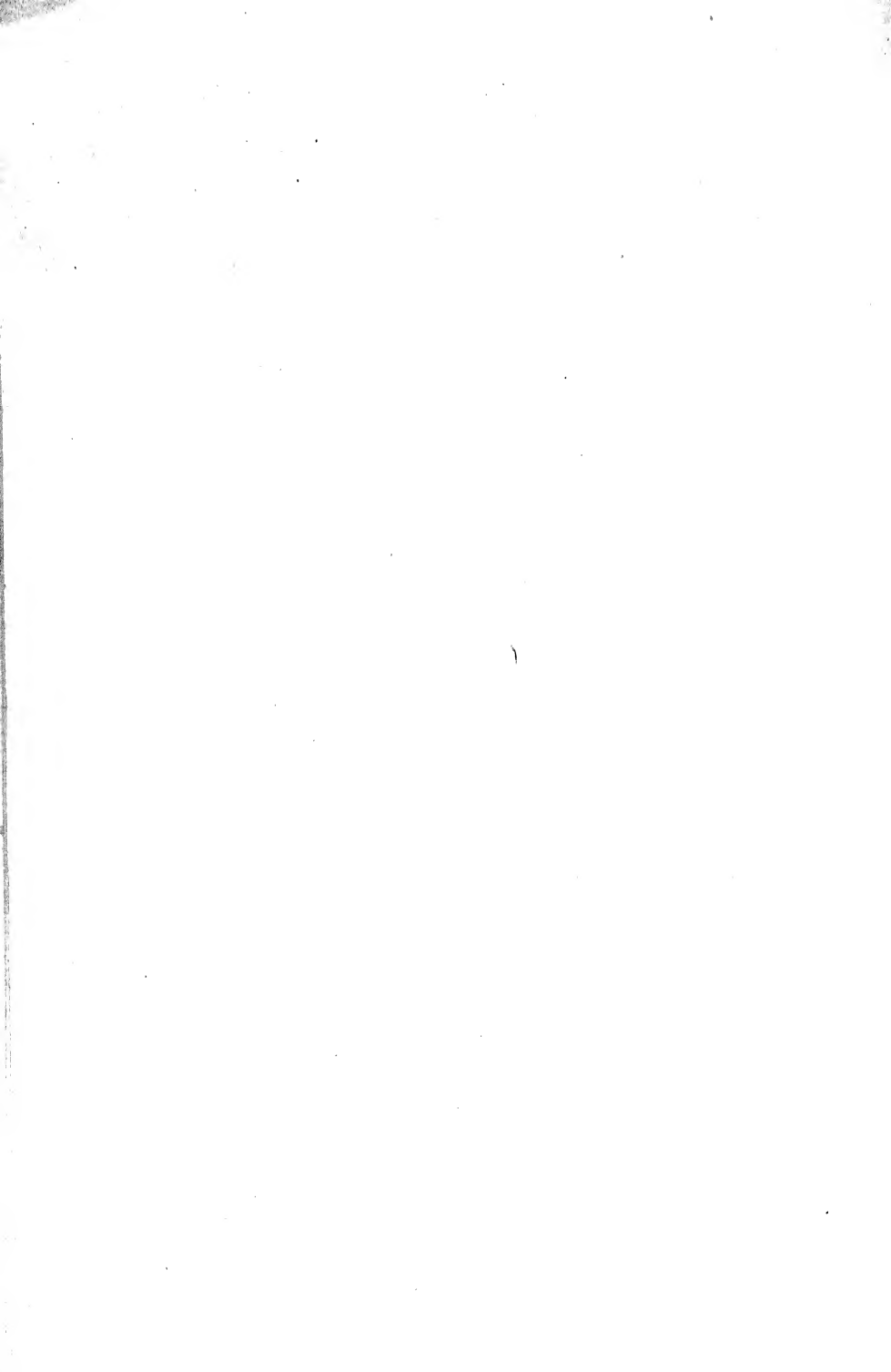




SPECTROSCOPY AND COMBUSTION THEORY



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FOREWORD

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THE issues of war may be determined by the superiority of the weapon, so in the struggle with Nature it is the instrument that wrests the secrets. The volcano and the bush fire struck awe in the heart of man, and wonder too, when he found the way to make use of fire. Flames still hide mysteries. The history of the progress of chemistry is knit closely with the study of combustion, even to the present day when 'reaction kinetics' are to the fore and many of the phenomena of combustion have been interpreted in terms of chain reactions. In flames, reactions are running fast and measurements of the kind which provide valuable information about slow oxidations cannot be made. The spectroscope, however, can reveal some of the constituents of flames and so can give a clue to what is happening, however fast the reactions may be, and may in many cases provide quantitative information about them. Such is the theme of Dr. Gaydon's book. Many will find useful a book which collects together what the spectroscope tells about flames.

Molecules may be excited by a variety of processes, and in returning to their normal states they will emit radiation. The excitation may come about as a result of collision with particles of high energy, moving fast because of the energy provided by the combustion, or as a result of electronic excitation during chemical changes. Other excited molecules or light absorption might also be responsible for the excitation. Whatever the means of excitation, it has to be remembered that if a certain emission spectrum is not obtained, it must not always be assumed that the radical or molecule corresponding to it is not present in the flame: the levels associated with its excitation may not allow an emission in the region investigated, or the conditions of excitation may not give rise to enough excited molecules.

There may be yet another reason, for, if an intermediate radical takes part in the reaction, there may never be sufficient of it present in the stationary state to provide an emission spectrum, even if the other conditions for emission are satisfied. Within such limitations, however, the spectra observed are often so characteristic that much new information can be got, which may be valuable in determining the mechanism of the flame reactions.

The late Professor Bone was determined to settle once and for all whether or not water was necessary for the combustion of carbon monoxide, and he eventually proved that dry carbon monoxide could burn. The spectroscope was used in that research, and illustrated very clearly the effect of the OH radical on the combustion. The work was done in these laboratories, and now Dr. Gaydon's recent researches on the banded spectrum of the carbon monoxide flame show that vibrational energy can be retained in the CO₂ molecules which are formed, a fact which seems to explain both the influence of moisture on the combustion and the mysteries known as 'afterburning'.

The centre of interest has now shifted perhaps to the combustion of hydrocarbons. The view that combustion occurred by successive stages of hydroxylation has had to undergo modification. In slow oxidations there is no doubt that peroxides are formed and that they influence the reaction; absorption spectra have helped to indicate their formation. There is much to learn yet as to what happens in the faster flame reactions: the spectroscope reveals some interesting bands. Are these attributable to the radical HCO? This is one of the many important problems which are discussed in this book, and by the elucidation of which, knowledge of flame reactions will be furthered.

A. C. EGERTON.

PREFACE

DURING recent years spectroscopy, both experimental and theoretical, has made useful contributions to combustion theory. Much valuable work has been done by individuals in several countries, but I think that in some cases a broader outlook on the subject might be beneficial. It is the purpose of this monograph to collect together and discuss the results of recent research in the several ways in which spectroscopy has been applied to combustion problems. Although brief sections devoted to the subject have appeared in various books such as Bone and Townend's *Flame and Combustion in Gases* and Herzberg's *Molecular Spectra and Molecular Structure*, there appears to be nothing solely devoted to the relations of spectroscopy and combustion. My own section in the Physical Society's Progress Report for 1941 provides a bibliography to most of the recent work, but is too brief to serve as more than a review of the subject.

The title of this monograph will probably, at first sight, call to the reader's mind the visible and near ultra-violet emission spectra of flames and explosions. This part of the subject does indeed occupy considerable space, as it is one which has received a great deal of attention, largely no doubt because of the relative ease of making simple empirical observations with quartz spectrographs. It is, however, also my purpose to cover a much wider field, including the infra-red region, the use of absorption spectra for following combustion processes, and the many less direct but none the less valuable applications of spectroscopy to combustion such as the derivation of the lifetimes of activated molecules, the lag in the equipartition of the energy liberated by the combustion processes, and the calculations of the heats of dissociation and thermodynamic quantities. The book aims at covering fairly fully the whole field of the applications of spectroscopy, both experimental and theoretical, to combustion theory, but in the cases where the applications are to chemical kinetics generally rather than to combustion in particular, the space devoted to

the work is limited. Perhaps rather more attention is paid to my own work on the afterburning and flame spectrum of carbon monoxide than might be given in a completely impersonal treatment of the subject, but I ask the reader's indulgence for this as, apart from the possible value of the work itself, I feel that it serves as a good example of the methods by which I hope to see more substantial contributions made by spectroscopy to the theory of combustion in the future.

I have endeavoured to present the subject in such a way that this monograph may be of service to those engaged in research in the field, but so that it may be read easily by the beginner and the non-specialist. The treatment is not mathematical, and where an understanding of the theory of molecular spectra is necessary I have tried to give this theory in simple terms. There is, of course, some overlapping in the various ways in which spectroscopic methods may be applied to the solution of combustion problems, but, on the whole, the subject divides itself naturally into a number of sections, and I have dealt with these as far as possible in such a way that each chapter may be read without reference to others; this should assist the casual reader who is interested in only a limited part of the subject.

I have included a fairly complete Bibliography and an Appendix giving details useful for the recognition of spectra frequently encountered in combustion work, and a list of the chief characteristics of the flame spectra which have been studied to date. This should make the book of some service for purposes of reference.

I wish to express my sincere thanks to Professor Egerton for his interest and encouragement, to Dr. W. G. Penney for valuable discussion on several points, to Dr. W. Jevons for suggestions relating to the typographical presentation, and to my wife for assistance with the proof-reading and preparation of figures. I am also much indebted to the Trustees of the late Viscount Leverhulme for the Research Fellowship, during the tenure of which I have written this monograph.

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GENERAL INTRODUCTION

PERHAPS the chief distinction between combustion and ordinary chemical reaction is the appearance of flame, that is the emission of light. It is therefore natural to expect that the study of the quality and quantity of light emitted by flames should form an important part of the study of combustion processes. Examinations of the quality, that is the spectrum, of the light from simple flames, were indeed among the first of spectroscopic observations. Mere observation of the spectrum and recording of the wavelengths characteristic of any type of flame can however contribute little to the theory of the combustion. It was not until after the systematisation of atomic spectra following the advent of the quantum theory and the subsequent interpretation of some of the complexities of molecular spectra, that real value was attached to the observation of flame spectra. The study of molecular spectra in the decade between 1920 and 1930 enabled the various characteristic banded spectra which are emitted by many flames to be assigned to definite emitters, many of them radicals such as CH, OH, C₂ and NH, whose presence in combustion processes, or even whose existence, had been unknown before the advent of the modern theory of molecular spectra.

The first chapter is therefore devoted to a quite elementary treatment of the theory of molecular spectra. This is given for the benefit of the reader who has not had a specialised training in spectroscopy, and the presentation given here has been made as simple as possible so that it may help readers who are only interested in the results of spectroscopy or in the practical applications of the subject and who have not had the opportunity to delve into the theory. This opening chapter is followed by one discussing the conditions under which emission spectra appear; some understanding of this is necessary if the interpretation of spectroscopic observations is to bear any relation to the facts. This second chapter lays stress on the quantity as well as the quality of the light emitted, and in this sense

provides the theoretical background for many of the quantitative investigations discussed in later chapters.

The next few chapters deal with the straightforward and obvious approach to the subject, the results of the study of the emission spectra of various flames and explosions being given in some detail. The probable emitter and the significance of the hydrocarbon flame bands, formerly known as the ethylene flame bands, is dealt with fully, and the origin and nature of the flame spectrum of carbon monoxide is also treated at some length. These chapters also include investigations of the spectra of cool flames, explosion flames, and of the internal combustion engine.

In recent years some interesting work has been done in following the progress of chemical reactions in the gas phase, such as slow combustion, by examining the absorption spectrum of the reacting gases. This has in some cases made a useful contribution to the understanding of the mechanism of the reaction, as by this method it is possible to follow the appearance of certain products quantitatively and in some cases to detect the presence of short-lived intermediary compounds which might otherwise have escaped notice. Chapter IX is devoted initially to a discussion of the advantages and limitations of absorption spectra for studying combustion problems, and then goes on to deal with the results obtained from the observation of the absorption of hydrocarbons undergoing slow combustion, and the contribution made by quantitative measurements to the kinetics of the reactions of OH radicals.

The bulk of the energy radiated by flames lies not in the visible and near ultra-violet, but in the infra-red. This region of the spectrum is, experimentally, rather less easy to study than the visible. Measurements of the infra-red emission from flames, especially quantitative measurements, have shown that there is a close relation between the infra-red radiation and the afterburning and so-called latent energy of the combustion. The results of investigations in the infra-red region are given in Chapter X, and the author's own researches and ideas on the afterburning are discussed fully in Chapter XII.

Chapter XI is devoted to the methods and results of calculating the lifetimes of activated molecules. This section of the subject, like those which follow in Chapters XIII and XIV, is of general interest to chemical kinetics, but the large energies

available from combustion processes and the big initial activation energies necessary for the reactions render the subject of especial importance to combustion.

In addition to results derived from the examination of the emission or absorption spectra of combustion processes, spectroscopy has contributed to the quantitative side of combustion theory in many less direct, but none the less important ways. Some of these are discussed in Chapters XIII and XIV, which deal with the calculation from spectroscopic data of thermodynamic quantities, such as specific heats, and the methods by which energies of dissociation are obtained from measurements of band spectra.

The last chapter, entitled "Kinetic Spectroscopy," endeavours to summarise the present contributions of spectroscopy to combustion theory, and to outline the ways in which future developments may be expected.

As stated in the Preface, the Bibliography and Appendix give information which may render the book of some service for reference purposes.

CHAPTER I

INTRODUCTION TO MOLECULAR SPECTRA

THE object of this chapter is to provide, as a background for the reader unacquainted with the theory of spectroscopy, a descriptive and entirely non-mathematical introduction to molecular spectra. This monograph is not, of course, intended to serve as a textbook on molecular spectra and it is necessary here, for the sake of brevity, to present the accepted facts and theories as bald statements without discussing the observations and theoretical developments which have led up to their adoption. For further details, and a much more able and complete treatment of the subject, the reader is referred to the books by Jevons ¹³⁴ and Herzberg ¹²³.

The most important observed spectra fall into two classes, those consisting of lines, which are now known to be emitted by atoms, and the banded, or as they were formerly called fluted, spectra which are now known to be due to molecules. In some cases regions of continuous spectrum are observed and these may be due to emission or absorption by atoms undergoing ionisation in the process or to molecules undergoing dissociation.

Line or Atomic Spectra.

The spectra emitted by many atoms, especially those in Groups I and II of the Periodic Table, appear fairly simple, but they nevertheless defied systematisation for a long time. Balmer first arranged the lines of the very simple hydrogen spectrum into a series, the original arrangement in terms of the wave-lengths of the lines being in a relatively complex form. The later realisation that it was the reciprocal of the wave-length, that is the wave-number (proportional to the frequency) of the light which was, for theoretical purposes, the more fundamental, enabled the wave-numbers of the lines of the hydrogen spectrum,

both of the visible series and of other series in the ultra-violet and infra-red, to be expressed in the simple form

$$\nu = R_H(1/n_2^2 - 1/n_1^2)$$

where n_1 and n_2 are integers such that $n_1 > n_2$ and n_2 takes the values 1, 2, 3, etc., and R_H is a constant known as the Rydberg constant for hydrogen.

Following this, it then became possible to arrange the spectrum lines of many other elements into series so that the wave-numbers could be expressed as the difference of two terms. The spectra of many elements being represented by a formula of the type,

$$\nu = R(1/(n_2 + a_2)^2 - 1/(n_1 + a_1)^2)$$

the Rydberg constant R having a value only very slightly different from that for hydrogen, and a_2 and a_1 being additional constants peculiar to the element whose spectrum is being considered.

Bohr Theory.

According to Bohr's theory, atoms and molecules can only exist in certain discrete energy states called stationary states which are selected by certain quantum conditions from the classically possible states. Thus for the hydrogen atom the electron may, classically, revolve around the nucleus in any form of ellipse, but on the Bohr theory the values of the major and minor half axes of the ellipse are restricted to certain values proportional to the squares of the natural numbers; the value for the number n for the major half axis takes the values 1, 2, 3, etc., and is known as the principal quantum number; the number l for the value of the minor half axis takes the values 0, 1, 2, etc., to $n - 1$, and is known as the azimuthal quantum number.

For atoms with more than one electron it is necessary to consider the resultant quantum number for the effect of all the electrons, and certain other features which affect the total energy of the atom, such as the spin of the electrons and the interaction with a magnetic field, are also restricted by quantum conditions, so that the energy state, or energy level, of any atom or molecule may be defined by assigning the values of the various quantum numbers.

According to Bohr, the emission or absorption of radiation occurs during the transition of the atom or molecule from one

energy state to another, that is, for atomic spectra, when an electron changes its orbit ; this marks the difference between the quantum theory and classical mechanics as, according to the latter, an electron moving in an orbit would radiate energy continuously, while on the quantum theory radiation only occurs when the electron changes its orbit. The relation between the frequency $\bar{\nu}$ of the radiation emitted to the energies E_1 and E_2 , of the two states of the atom or molecule is given by the well-known expression,

$$E_1 - E_2 = h\bar{\nu} = hc\nu$$

where h is a universal constant known as Planck's constant, c is the velocity of light and ν is the wave-number (in cm^{-1}). The energies E_1 and E_2 correspond to the terms used in expressing the series in line spectra. The Rydberg constant used in these expressions can be derived in terms of Planck's constant and the charge e on the electron and has the value

$$R = 2\pi^2 e^4 / ch^3 \times mM / (m + M)$$

where m and M are the masses of the electron and the atom respectively.

All possible transitions between the energy states of the atom are not possible, and this is expressed by a number of *selection rules* regulating the possible changes in the various quantum numbers ; these rules have to a large extent been derived empirically, but can also be obtained approximately by the *correspondence principle*, according to which the results obtained for high values of the quantum numbers must approach the results expected by classical mechanics.

Thus it will be seen that the line spectra characteristic of atoms are due to electronic transitions within the atom, and the first stage in the interpretation of the spectrum is to build up, from the spectrum, an energy level scheme for the atom.

The Spectra of Diatomic Molecules ; Vibrational Structure.

Many band spectra which lie in the visible and ultra-violet regions, such as, for example, the well-known Swan bands found in the inner cone of the Bunsen flame, show obvious regularity. The system consists of a number of bands with sharp edges or heads on one side, and shaded off, or degraded, on the other

side. When the spectrum is examined under high dispersion, that is big magnification, each band is seen to consist of a number of fine lines.

It is known that the position of the band system as a whole is determined by the electronic energy change, that is band spectra in the visible and ultra-violet are due to electronic transitions. The electronic energy levels of molecules are usually fewer than those of atoms, so that the number of band systems observed is much less than the number of lines observed for an atom. In only a few cases has it been possible to arrange the systems into series corresponding to the Rydberg series of line spectra.

The gross structure of a band system, that is the splitting of the system into a number of bands, is due to the contribution to the energy of the molecule made by the vibration of the atoms along the internuclear axis. Treating the molecule as a harmonic oscillator, it is found that the vibrational energy is quantised and takes values given by the product of the vibrational frequency, Planck's constant and the vibrational quantum number v . This quantum number takes half-integral values $\frac{1}{2}$, $1\frac{1}{2}$, $2\frac{1}{2}$, etc., but it is usually convenient in practice to suppress this fact by using integral values and inserting the actual energy difference between the vibrational levels of lowest energy for the two electronic states instead of the change in electronic energy itself. Thus each electronic energy level of the molecule will be split into a number of vibrational levels with energy given by

$$E = E_e + v \cdot \omega$$

v being the vibrational quantum number, ω a constant dependent on the vibrational frequency (usually referred to loosely as the vibrational frequency itself), and E_e is the electronic contribution to the energy. Taking into account deviations from the simple harmonic vibration of the molecule

$$E = E_e + v \cdot \omega - v^2 \cdot x\omega + v^3 \cdot y\omega + \text{etc.}$$

For electronic transitions all changes of the vibrational quantum number are permitted so that the positions of the bands of the system may be expressed by the formula

$$\begin{aligned} \nu &= E_e' + v' \cdot \omega' - v'^2 \cdot x' \omega' + \text{etc.} \\ &- (E_e'' + v'' \cdot \omega'' - v''^2 \cdot x'' \omega'' + \text{etc.}) \end{aligned}$$

where the primes ' and " refer to the upper and lower electronic energy levels respectively.

In making the vibrational analysis of a band system it is usual to try to arrange the bands into an array between the values of the initial and final vibrational quantum numbers v' and v'' . Any band is then referred to by the values of the quantum numbers as the (v', v'') band. The wave-lengths λ , wave-numbers ν and intensities I for the strong bands of the well-known Swan system of C_2 are given in Table 1 (from Jevons¹³⁴), and the wave numbers are then arranged in Table 2 in an array of the type mentioned. In this table the differences between the wave-numbers of the bands are printed in italics.

TABLE 1.—STRONG HEADS OF THE SWAN SYSTEM OF C_2 .

λ	ν	I	λ	ν	I	λ	ν	I
6191.2	16147	3	5501.9	18171	4	4697.6	21282	7
6122.1	16330	4	5165.2	19355	10	4684.8	21340	4
6059.7	16498	3	5129.3	19490	6	4382.5	22812	2
5635.5	17740	8	5097.7	19611	1	4371.4	22870	4
5585.5	17899	8	4737.1	21104	9	4365.2	22902	5
5540.7	18043	6	4715.2	21202	8			

TABLE 2.—VIBRATIONAL SCHEME FOR THE HEADS OF THE STRONG BANDS OF THE SWAN SYSTEM.

$v' \backslash v''$	0		1		2		3		4
0	19355	<i>1615</i>	17740	<i>1593</i>	16147				
	<i>1749</i>		<i>1750</i>		<i>1752</i>				
1	21104	<i>1614</i>	19490	<i>1591</i>	17899	<i>1569</i>	16330		
	<i>1708</i>		<i>1712</i>		<i>1712</i>		<i>1713</i>		
2	22812	<i>1610</i>	21202	<i>1591</i>	19611	<i>1568</i>	18043	<i>1545</i>	16498
			<i>1668</i>		<i>1671</i>				<i>1673</i>
3			22870	<i>1588</i>	21282				18171
					<i>1620</i>				
					22902	<i>1562</i>	21340		

It may be seen that the differences in any row, vertical or horizontal, are not far from constant, and that the wave-numbers of the bands may be expressed with reasonable accuracy by the formula

$$\nu = 19355 + 1770 v' - 20 v'^2 - (1625 v'' - 11.5 v''^2)$$

which is of the form given above, so that we see that the constants 1770 and 1625 correspond approximately to the vibrational frequencies ω' and ω'' of the molecule in the two electronic states.

It is customary to use the symbols ω_e and $x_e\omega_e$ for the values of ω and $x\omega$ as defined above when these are calculated for infinitesimal amplitude (pure electronic energy); when insufficient data are available for calculating ω_e the value of $\omega_{1/2}$, the energy separation between the two lowest vibrational levels, is frequently given.

The bands which fall in diagonal rows often form close groups, and these are known as *sequences*; thus the (0, 0), (1, 1) and (2, 2) bands at 19355, 19490 and 19611 cm^{-1} form such a sequence. Bands in the vertical and horizontal rows form more widely spaced series known as *progressions*; the (0, 0), (0, 1) and (0, 2) bands at 19355, 17740 and 16147 form such a progression, all the bands having $v' = 0$, and hence this is known as the $v' = 0$ progression.

If all the bands of a system can be arranged into a scheme such as that of Table 2, then it is usually safe to assume that the emitter is a diatomic molecule. The value of the vibrational frequency depends on the binding force between the two atoms of the molecule and on their mass, and comparison of the vibrational frequency with those known for other molecules is often of great help in identifying the molecule responsible for the band system.

In making a vibrational analysis it is sometimes necessary to take into account certain refinements for which the reader is referred to the larger books on the subject. The scheme in Table 2 is drawn up from data for band heads; correctly, data from band origins should be used. The electronic energy levels are in some cases split into two or more components by the spin of the electrons; this may complicate the vibrational structure. It is a general but not quite invariable rule that the bands are degraded in the same direction as the vibrational structure; thus if $\omega' > \omega''$ the bands are shaded to the violet, and if $\omega' < \omega''$ the bands are shaded to the red. This is often of assistance in making the analysis. When one or both of the atoms of the molecule possess isotopes of comparable abundance, the bands of the spectrum are all split into components due to the various isotopes; the vibrational frequency of the molecule is proportional to the square root of the force constant divided by the reduced mass $\frac{M_1 M_2}{M_1 + M_2}$, and hence measurements of this isotope

splitting of the band heads are often decisive in fixing the emitter of the system.

Rotational Structure of the Spectra of Diatomic Molecules.

The fine, line, structure of individual bands, such as that which can be seen for the spectra of CH and OH in the plates, is due to the rotation of the molecule about its centre of gravity.

For the simplest type of electronic level, that known as $^1\Sigma$, the extra energy of the molecule due to its rotation may have the values given by the expression

$$E_r = B.J(J+1)$$

or with greater accuracy by

$$E_r = B.J(J+1) + D.J^2(J+1)^2 + \text{etc.}$$

where J is the rotational quantum number and B and D are constants; B depends on the moment of inertia and has the value

$$B = h/8\pi^2 cI$$

where the moment of inertia, I , is the product of the reduced mass $\frac{M_1 M_2}{M_1 + M_2}$ and the square of the internuclear distance. The constant B is usually written as B_0 or B_e , according to whether it refers to the lowest vibrational level or to the completely vibrationless state of the molecule.

It is found that for a transition between two such $^1\Sigma$ states the change ΔJ of the rotational quantum number is restricted to the values ± 1 . Thus, using the primes ' and '' to refer to the upper and lower electronic states respectively, the lines of any one band with origin ν_0 are given by

$$\nu = \nu_0 + B'.J'(J'+1) - B''.J''(J''+1)$$

or, since $J' = J'' \pm 1$,

$$\nu = \nu_0 + B'(J''+1)(J''+2) - B''.J''(J''+1)$$

or

$$\nu_0 + B'(J''-1)J'' - B''.J''(J''+1)$$

so that the lines of the spectrum fall into two series or branches, known as the P and R branches respectively. It can be shown by a little arithmetical manipulation of these formulae that if $B' = B''$ the two branches consist of lines all separated by $B' + B''$ from each other, the branches forming a continuation of each other apart from a single missing line at the origin ν_0 . If, however, $B' > B''$, the lines of the P branch start at the origin with

corresponding to $J = \pm 2$ or even more are observed, and each branch may be split into two or more components according to the multiplicity of the electronic terms. The value of the moment of inertia determined from the rotational structure is of great help in determining the emitter; thus hydrides have a very small moment of inertia which distinguishes them at once from heavier molecules. The detailed examination of the rotational structure also enables the type of the electronic terms to be determined.

Electronic States of Diatomic Molecules.

The electronic state of a molecule is described by two quantum numbers. Λ is the resultant orbital angular momentum of the electrons along the internuclear axis, and corresponds to the azimuthal quantum number for atoms; it takes the values 0, 1, etc., and according as this value is 0, 1, 2, etc., the electronic state is referred to by the Greek letters Σ , Π , Δ , etc. The other quantum number of importance is the resultant spin of the electrons, S , which takes half integral values; this determines the multiplicity $M = 2S + 1$ of the state. Thus any state is represented by the multiplicity, written as a superscript on the left, and its Λ value, so that a ${}^3\Pi$ (read triplet pi) state has $M = 3$ ($S = 1$) and $\Lambda = 1$.

These quantum numbers Λ and S combine with each other and with the rotational quantum number in several ways described by Hund as cases a , b , c and d , and give rise to a set of energy levels. Thus in Hund's case a , Λ and S form a resultant Ω , and the rotational energy levels may be expressed in the form

$$B[J(J+1) - \Omega^2]$$

where J can take the values Ω , $\Omega + 1$, $\Omega + 2$, etc. Thus, for example, a ${}^2\Delta$ state, for which $\Lambda = 2$ and $S = \frac{1}{2}$, consists of two sublevels with $\Omega = 1\frac{1}{2}$ and $2\frac{1}{2}$, the values of J being $1\frac{1}{2}$, $2\frac{1}{2}$, $3\frac{1}{2}$, etc., for the first and $2\frac{1}{2}$, $3\frac{1}{2}$, $4\frac{1}{2}$, etc., for the second. Thus the levels corresponding to $J = \frac{1}{2}$ and to $J = \frac{3}{2}$ and $1\frac{1}{2}$ are absent from the first and second sublevels respectively; this results in the spectrum of a band involving a ${}^2\Delta$ level having some additional missing lines near the origin.

There are some selection rules governing the possible electronic transitions. Λ may change by 0 or ± 1 only, and the multiplicity does not change at all for strong band systems, but weak systems

are known corresponding to a change of ± 2 in M . The following are examples of permitted transitions,

$${}^1\Sigma \rightarrow {}^1\Sigma, {}^2\Sigma \rightarrow {}^2\Sigma, {}^1\Sigma \rightarrow {}^1\Pi, {}^1\Pi \rightarrow {}^1\Sigma, {}^2\Pi \rightarrow {}^2\Delta$$

and the following would not be allowed

$${}^1\Sigma \rightarrow {}^1\Delta, {}^3\Sigma \rightarrow {}^3\Delta, {}^1\Sigma \rightarrow {}^5\Sigma.$$

When Δ does not change (i.e. $\Sigma \rightarrow \Sigma$, $\Pi \rightarrow \Pi$, etc.) the band consists of strong P and R branches, and the Q branch is absent or consists of only a few lines. If Δ changes by ± 1 (i.e. $\Sigma \rightarrow \Pi$, etc.), then the bands show a strong Q branch, which is roughly twice as strong as the P and R branches.

Further discussion of electronic states is beyond the scope of this chapter, and the reader is again referred to the books by Jevons and Herzberg, or to Mulliken's papers^{180 181 182}. It will be seen, however, that a sufficiently detailed study of the fine structure of a band, including observation of the number of missing lines near the origin and the number, type and intensity distribution of the branches into which the lines can be arranged, enables the electronic transition to be determined unambiguously. Knowledge of the types of electronic state involved may bear on the combustion problem in several ways. Firstly, since molecules with an even number of electrons only have electronic terms of odd multiplicity and vice versa, the multiplicity gives a check on the identity of the molecule. Secondly, if molecules reach a state from which transitions to the ground electronic state are forbidden by one of the selection rules, then the activated molecules will have a long life and can only lose their energy by collision, which may activate some other reaction process. Thirdly, knowledge of the type of electronic state may, with the help of the Wigner-Witmer correlation rules (see page 141), enable the nature and states of the dissociation products to be determined.

Vibrational Intensity Distribution; the Franck-Condon Principle.

We have seen that the gross structure of a band system is determined by the internal vibration of the molecule, and have stated that for a diatomic molecule the change of the vibrational quantum number is unrestricted. It is now proposed to discuss the factors determining the relative intensities of the bands of

a system. The intensity of any one band depends on the population of the initial state, that is the number of molecules with that initial value of the vibrational quantum number, v' for emission or v'' for absorption, and on the transition probability. The population depends on the energy of the state and the temperature, being given, in thermal equilibrium, by the Maxwell-Boltzmann distribution law (see page 132). The transition probability depends, among other factors, on the relative positions of the potential energy curves for the molecule in the two electronic states.

The potential energy curve of a diatomic molecule in a stable

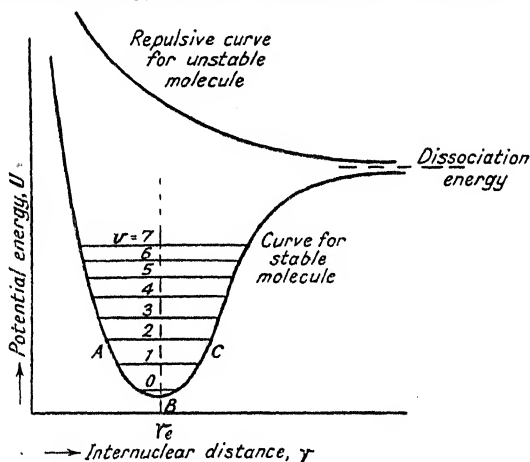


FIG. 3.—Potential energy curves of a diatomic molecule.

electronic state takes the form shown in Fig. 3 (lower curve); the potential has a minimum at the equilibrium internuclear distance r_e , rises steeply as the atoms are brought closer together because of the strong repulsion between the atoms when very close, and rises to a limit, the *dissociation energy*, as the atoms are drawn apart. The molecule can only exist in a number of discrete vibrational energy levels, represented by the horizontal lines in the figure and indicated by the vibrational quantum numbers v . A molecule in any state, say $v = 3$, may be considered as executing an approximately simple harmonic vibration about the equilibrium position so that the internuclear distance and potential energy trace the path ABC, the fall in the potential energy at B corresponding to the gain in kinetic energy due to

the relative motion of the atoms. The vibrational energy levels are approximately evenly spaced for low values of v , but close up as the dissociation limit is approached. The potential energy curve may be calculated approximately from the values of the vibrational frequency and the moment of inertia obtained from the analysis of the spectrum. The upper curve in Fig. 3 shows the type of curve which represents the potential energy of two atoms which do not form a stable molecule. It is sometimes referred to as a repulsive state of the molecule, and an electronic transition to such a state results in dissociation, and the spectrum is continuous instead of banded.

For an electronic transition the distribution of intensity

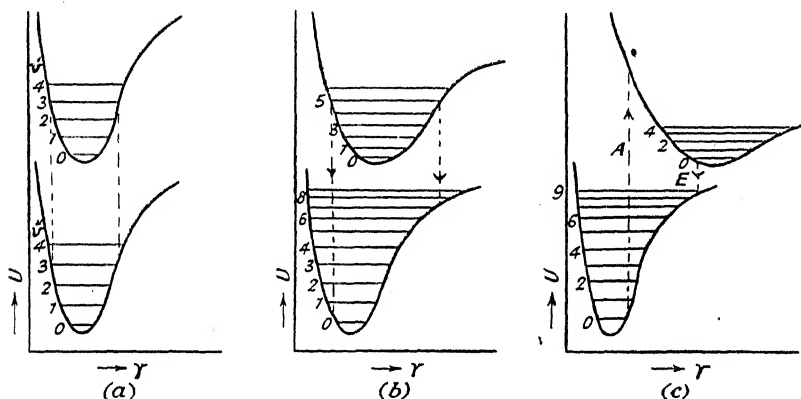


FIG. 4.—Relative positions of potential energy curves.

among the various bands of the system depends on the relative positions of the potential energy curves in the two electronic states. Fig. 4 shows three such relative positions. If it is assumed that the electronic transition takes a time which is small compared with the time for the movement of the heavier atoms, then it follows that the internuclear distance r will not change appreciably during the transition. Classically, it may be seen that for a simple harmonic vibrator the atoms spend longest at either end of their path, so that the most probable values of r are the maximum and minimum ones for the molecule in the state from which the transition is occurring. In Fig. 4 (a) the potential curves are drawn roughly the same shape and with one immediately above the other. Considering a level of the upper state,

say $v' = 3$, it will be seen that the ends of this level lie immediately above those for the same value of v'' in the lower state, that is $v'' = 3$. Thus the most probable transition from the $v' = 3$ level is to $v'' = 3$, and so on, so that the band system corresponding to two potential curves so arranged must show a strong sequence of bands (0, 0), (1, 1), etc.

With the curves slightly displaced as in (b) it will be seen that the ends of, say, the level $v' = 5$ come over the ends of the levels $v'' = 1$ and $v'' = 7$, so that the strongest bands with initial level $v' = 5$ will be the (5, 1) and (5, 7). Extending this it can be shown that, if the bands are arranged in an array of the type of Table 2, the strongest bands will be those which lie on a curve of roughly parabolic form. This is usually referred to as a Franck-Condon parabola. When the relative position of the curves approaches (a) the parabola is narrow and lies about the $v' = v''$ sequence, that is, the (0, 0), (1, 1), etc., bands are strong. When the position of the curves approaches (c) the Franck-Condon parabola becomes very open, so that the spectrum shows long progressions, the $v' = 0$ progression often being strong in emission and the $v'' = 0$ in absorption. This may be seen from (c); in absorption the most highly populated level will be that with $v'' = 0$, and transitions from this will only occur to high values of v' or even to dissociation, while in emission most of the molecules will start from $v' = 0$ and transitions will occur to high values of v'' (8, 9, 10, etc.). It will also be noticed that emission corresponds to the small energy change E , so that the emission spectrum tends to lie to long wave-lengths, while the strongest bands in absorption correspond to a big energy change A and will lie to shorter wave-lengths. This subject will be referred to again when discussing the emitter of the carbon monoxide flame bands and the afterburning and latent energy of combustion of carbon monoxide in Chapters VI and XII.

The above simple treatment of the Franck-Condon principle and intensity distribution gives results which agree qualitatively with experiment. To obtain closer agreement between theory and observation, refinements in the theory are necessary, and a wave-mechanical treatment such as that given by Gaydon and Pearse²⁴ for the rubidium hydride molecule must be used. This shows that in addition to the main Franck-Condon parabola, weaker secondary, tertiary, etc., parabolae are formed.

Infra-red and Raman Spectra.

Bands are observed in both the emission and absorption spectra of many molecules in the near infra-red (around 2 to 20 μ). These are due to change of the vibrational and rotational energies of the molecule only, the electronic state being unchanged ; such spectra are referred to as *vibration-rotation spectra*. For diatomic molecules it is found that only heteronuclear molecules give these spectra and that then for strong bands the vibrational quantum number changes only by one unit. For homonuclear molecules (N_2 , O_2 , H_2 , etc.) theoretical considerations show that such changes of vibrational quantum number are ruled out on grounds of symmetry ; this has received little attention in relation to combustion, but since vibrationally activated molecules of O_2 , N_2 , etc., cannot lose their energy by radiation, they must lose it by collision, and may thus act as energy carriers in chain mechanisms.

Absorption spectra in the far infra-red have also been observed for a few molecules. These rotation spectra, as they are called, are due to changes in the rotational energy only.

When a beam of monochromatic light (that is light of one wave-length) is scattered, it is found that the scattered light consists of, in addition to the original wave-length, other wave-lengths which correspond to the original frequency less the natural vibrational frequencies of the scattering substance. Both this effect, which is known by the name of its discoverer, Raman, and observations of the infra-red spectrum, are used to determine the vibrational frequencies of the molecule. Such determinations have little direct bearing on combustion, but are of great importance in chemistry, especially organic chemistry, in deciding on the structure and character of molecules. The knowledge of the vibrational frequencies is also necessary for the calculation of various thermodynamic quantities, such as specific heats, and also has a bearing on the activation energy necessary for chemical reaction to proceed.

Spectra of Polyatomic Molecules.

By far the greater number of emission spectra are known to be due to diatomic molecules, but a few systems are known which are emitted by triatomic or polyatomic molecules, and others are known in absorption. It appears that most of the excited elec-

tronic states of polyatomic molecules are unstable, and hence the spectra corresponding to transitions involving such states are not obtained in emission, and in absorption only a continuum is obtained. Such polyatomic spectra as have been observed are very complex, and although a few, such as those of ClO_2 and benzene, show obvious regularity and are capable of at least a partial analysis, this is not generally true. Apart from a few linear molecules, which can be treated in a way similar to diatomic molecules, little is known of the electronic or rotational structure of such spectra. The vibrational analysis is complicated by the greater number of vibrational frequencies; triatomic molecules have three possible modes of vibration, and in general an N -atomic molecule has $3N-6$ modes, although the actual number observed may be reduced if the molecule possesses much symmetry. Attempts have been made to derive the vibrational selection rules for electronic transitions by Herzberg and Teller ^{123b} and Ku ¹⁵⁷, which suggest that only certain of the possible bands are allowed, but this seems at variance with observations on the absorption spectrum of SO_2 , and developments in the theory will probably have to await further experimental work.

The study of the infra-red spectra of polyatomic molecules has made better progress, and in many cases the vibrational frequencies have been derived from observations of the infra-red and Raman spectra, and from these the shape and structure of the molecule can be calculated. Thus CO_2 is known to be linear, while SO_2 and H_2O are isosceles triangles. The infra-red spectra of polyatomic molecules have been treated theoretically by Dennison ⁴⁹, and a section is devoted to polyatomic molecules by Sponer ²²¹, and a textbook on the subject by Herzberg is in preparation. Mulliken has recently published a number of papers (in *Phys. Rev.* and *J. Chem. Phys.*) on the electronic structure of polyatomic molecules.

CHAPTER II

CONDITIONS GOVERNING THE APPEARANCE OF EMISSION SPECTRA

FOR the production of an emission spectrum several requirements must be satisfied, and consideration to all these should be given before any conclusions are drawn regarding the concentration of a particular molecular species in a flame or other source. Obviously there must be a sufficient concentration of the molecules present for a strong emission spectrum to be observed, but it is found that very small concentrations may be enough to give a relatively intense emission spectrum, provided this spectrum is not masked by that of a more abundant substance. Thus the spectrum of the nitrogen afterglow almost invariably shows as one of its strongest features the β band-system of nitric oxide, even though great care may have been taken to free the nitrogen from all trace of oxygen-containing compounds.

An emission spectrum of an atom or molecule can, of course, only be observed if the electronic energy levels are so spaced that a transition may occur for which a line or band system lies in the spectral region being studied ; the further reservation must be made that the source possesses sufficient energy to excite the atom or molecule to the required extent. Thus although we know that N_2 , O_2 , and CO molecules are present in considerable quantities in flames, the only electronic transitions for these molecules which give rise to band systems in the visible or quartz ultra-violet involve highly excited states ; thus spectra of these molecules are not observed in emission from flames, although, of course, such spectra occur readily in more vigorous sources such as discharge tubes. It may well be, therefore, that in addition to the well-known radicals such as CH , C_2 , OH , which are found by their emission spectrum to be present in flames, other radicals, such as perhaps CH_2 , may exist, but their observation by emission spectra is prevented by the absence of a stable electronic state

with energy not too much above that of the ground state. Thus, failure to obtain spectroscopic evidence for the presence of an unknown radical should not preclude its use in combustion equations. In some cases it might be possible to predict the energy levels of such a molecule, and in these cases the presence or absence of an emission spectrum would, other conditions being fulfilled, prove crucial.

Sources ; Emission from Flames.

The type of spectrum emitted depends considerably on the source used. This dependence is due not only to the limits on the amount of energy available, but also to the manner in which excitation is produced. In sources such as discharge tubes and arcs the excitation is mostly by fast electrons which have been accelerated by the electric field, and the energy which they carry is sufficient to excite spectra corresponding to transitions between electronic states of high energy and even to excite spectra due to ionised molecules and atoms. In flames the excitation of the molecules is due chiefly to either thermal causes or to chemiluminescence, and in either case the energy available is very limited, so that the spectra observed correspond invariably to transitions between states of low energy. All the band spectra produced by flames which have been analysed correspond to transitions to the ground electronic state.

When a fast electron strikes a molecule, the tendency is for the electrons of that molecule to be disturbed, but for the relatively light electron to have little effect on the positions or motions of the heavier atomic nuclei. Thus, in sources in which excitation is chiefly by electron impact, the electronic states to which the molecules are most often promoted are those whose equilibrium internuclear distances are not very different from the equilibrium distance in the ground state, i.e. the potential energy curves resemble those shown in Fig. 4 (a) (see page 15); band systems which correspond to a big change in the internuclear distance do not appear readily in discharge-tube or ordinary arc sources; as examples of this effect may be quoted the Schumann-Runge band-system of oxygen and the β bands of nitric oxide which do not appear as readily in simple uncondensed discharges as in some other sources.

In thermal excitation it is probable that collisions between

particles of molecular or atomic masses are most effective in producing the excitation. It is true that there is a certain amount of ionisation in flames, but the actual concentration of free electrons is very small, and such electrons as are present will not, in the absence of an electric field, have very high energies. For collisions between molecules of comparable mass there is a greater chance of the excitation of one of the molecules to an electronic state in which the nuclear separation is different from its initial value. This assumption seems to be justified experimentally by the observation in flame sources of band systems which do not appear readily in other sources in which excitation is by electron impact. Thus Gaydon and Pearse⁹³ observed bands due to NiH in a flame into which nickel carbonyl had been introduced, but the bands have not been observed in discharge-tube sources or in an arc in hydrogen, although the bands have since been obtained in absorption in furnaces containing nickel and hydrogen, indicating that some NiH molecules should be produced under the conditions of the discharge tube or arc; the analysis of the bands shows that they are strongly degraded to the red, the equilibrium internuclear distance increasing from 1.48 Å. in the ground electronic state to 1.73 Å. in the upper state. Similarly the carbon monoxide flame spectrum has not, apart from the rather special case of the afterglow, been observed in emission in a discharge tube; this may be explained if there is a big change in the shape or size of the CO₂ molecule (see page 59).

Some spectra are observed in flames more readily than in other sources for what is probably a different reason. These spectra are mostly due to molecules which are chemically reactive, and do not exist as stable substances outside the flame. It seems that in some cases the combustion processes in flames produce these molecules so that a higher concentration is maintained than would normally be the case. Thus Hedfeld¹¹² has observed the spectra of the mono-halides of some of the alkaline earth metals, such as CaI and SrBr, readily in flames, although they are difficult to obtain in arc sources. Easily decomposed polyatomic molecules appear to be less easily destroyed in flames than in more vigorous sources such as arcs and powerful discharges, and in this respect flames resemble more the much milder Tesla type of discharge, which is, however, able to excite rather higher electronic levels than the flame.

In cool flames, such as that of ether, when the temperature of the reacting gases is quite low, it is clear that the emission of light cannot be due to thermal causes, but must be a chemiluminescent effect. The molecules are either formed in an already excited electronic state, so that a number of them are able to radiate directly without the need for any outside supply of energy, or else the molecules are the recipients of a large amount of energy from some other body which has been involved in the combustion process and has retained the bulk of the energy of the chemical reaction. To what extent chemiluminescence is responsible for the emission of light from ordinary flames is a debatable point. At one time the opinion that the radiation from flames, especially the infra-red radiation, depended solely on temperature effects seemed fairly general, but such quantitative measurements as have been made (e.g. Kondratjew ¹⁴⁸) seem to indicate that this is not so and that at least a large part of the radiation from flames is of a chemiluminescent character. The author is not aware of any actual observations on the appearance of gases at temperatures as high as, say, 2000° C., but it is frequently stated that no visible or ultra-violet radiation is obtained from heated gases, which would indicate that most if not all of the radiation from flames is chemiluminescence. Such a conclusion would have far-reaching effects on the application of the study of the emission spectra of flames to combustion. If the radiation is of a chemiluminescent character, then, firstly, the combustion theory should be able to offer an explanation of the formation of such radicals as OH, C₂, CH in excited electronic states. Secondly, it means that the most minute stationary concentrations of these substances may be enough to maintain a strong emission, as all the molecules may be formed in the excited state instead of only a small proportion of the normal molecules being excited by thermal means. The rôle played by chemiluminescence is, however, still uncertain; in some cases, such as perhaps for OH, the effect appears to be important, while in other cases, for example CH (see page 38), it seems that thermal excitation plays at least some part in producing the emission.

There may also appear to be the possibility of the spectrum of a substance being excited by fluorescence by the ultra-violet light from the flame itself. However, observations on the

absorption spectra of flames show that they are remarkably transparent to visible and ultra-violet light, so that fluorescence cannot play an important part in exciting the emission spectra of flames. The absence of strong absorption by the flame also means that the emission spectrum will not be weakened appreciably by self-absorption. Using very high resolving power or a spectrum line reversal method, it is possible to observe the absorption by the OH radical corresponding to the 3064 Å. band; thus the OH radiation must be slightly weakened, but the effect is probably too small to seriously affect results based on quantitative measurements of the amount of OH radiation, but calculation of the effective temperature of the molecules by observation of the rotational intensity distribution might be complicated by this self-absorption. In the infra-red the self-absorption is stronger, but is still not of major importance, although the contour of the $4.4\ \mu$ emission band of CO_2 is apparently affected, and pre-heating in advance of the flame-front, caused by the absorption of infra-red radiation from the flame itself, may be of some importance in determining flame speeds.

Radiative Lifetime, Collisions, and Emission.

As has already been shown, the emission spectrum emitted by a particular molecular species depends on the concentration of the molecules, the arrangement of the electronic energy levels, the amount of energy available for the excitation of the molecules to these levels, and on the method of excitation. There is at least one other factor of great importance which may easily be overlooked. That is the after-history of the excited molecules. This depends on the electronic transition probability, which determines the radiative life of the molecule, and on the chances of loss of energy by collision processes, which may be termed the collision life.

The radiative life of an excited molecule, that is the average time before the molecule loses its energy by radiation, may vary very considerably according to the particular electronic transition involved, the life usually being greater than 10^{-8} sec., but sometimes much greater. At atmospheric pressure the time between collisions for a particular molecule is of the order 10^{-10} sec., so that an excited molecule with even a high electronic transition probability will make about 100 collisions on the

average before there is sufficient time for it to lose its energy by radiation, and for less favoured transitions the number of collisions may be several orders higher. Thus if the collisions are effective in deactivating the molecules the amount of radiation emitted will be very much reduced. Three examples will serve to illustrate the important effect of the transition probability and of collisions in determining the strength of an emission spectrum.

The cyanogen radical CN possesses two band systems, known as the Red System and the Violet System. Both these correspond to transitions to the ground electronic state, the red system requiring an excitation energy of around 1.4 electron volts, and the violet system about 3.2 e.v. One might therefore expect, judging from this information only, that the red system would appear more easily. Actually, the bands of the red system are rarely noticeable at all in flames or ordinary discharge tubes, although the violet CN bands are very easily obtained in these sources, being indeed among the most persistent of band systems and giving one of the most sensitive tests for the presence together of carbon and combined nitrogen. It is known that the violet system has a high transition probability (see page 105), and it may be assumed that the red system, although corresponding to an allowed ${}^2\Pi \rightarrow {}^2\Sigma$ transition, has a low probability which gives the molecules sufficient time to be deactivated by collision. The reason for the low transition probability is, in this case, probably the big difference in the distance between the C and N atoms in the two electronic states, there being little overlap between the wave-functions in the two states.

As a second example may be taken the First and Second Positive band-systems of nitrogen. These correspond to the transitions $B^3\Pi$ to $A^3\Sigma$ and $C^3\Pi$ to $B^3\Pi$, respectively, so that the final state of the Second Positive is the initial state of the First Positive bands. Neglecting deactivation by collision the First Positive system should therefore always be stronger than the Second Positive system, since any molecule which has just undergone the transition $C^3\Pi \rightarrow B^3\Pi$ should then be in a position to undergo the further transition $B^3\Pi \rightarrow A^3\Sigma$. In discharge tubes containing pure nitrogen, the two band systems are indeed found to be of comparable intensity, and the discharge is coloured bronze, owing to the strong red and yellow light emitted for the

First Positive system blending with the violet light characteristic of the Second Positive system. In discharges through air, however, the colour of the discharge is not bronze but violet, and the Second Positive bands dominate the spectrum. This remarkable change in the relative intensity of the two systems caused by the presence of some 20% of oxygen may be taken to indicate that the oxygen molecules are much more effective than nitrogen in deactivating by collision the N_2 molecules in the $B^3\Pi$ state. This is, therefore, a good example of the selective action of different gases in deactivating by collision, oxygen being more effective than nitrogen, and the effect on the $B^3\Pi$ state being greater than on the $C^3\Pi$ state.

The third example we shall consider is that of the Cameron bands of carbon monoxide. These bands are due to a transition from a $^3\Pi$ state to the ground $^1\Sigma$ state, the transition probability being low owing to the change of multiplicity. The emission bands of this system lie in the region 2000–2500 Å. The bands are not usually obtained in flames or ordinary discharge tubes, although the energy in the latter source is certainly more than sufficient for their excitation. Hansche¹⁰⁸ has found that the system is produced best in a discharge at low pressure in a vessel of large dimensions, the most favourable pressure range being from 0.003 to 0.002 mm. The reason for this is fairly obviously that the low pressure reduces the number of collisions, so that the excited molecules are given a better chance to lose their energy by radiation.

These examples suffice to show that the emission spectrum of any molecule is governed to a considerable extent by the transition probability for the particular electronic rearrangement concerned, and that the number and nature of the collisions which the excited molecule may suffer are also of importance in determining the quantity of radiation emitted. The methods of deriving the radiative and collision lives, and some results obtained from such considerations are discussed more fully in Chapter XI.

Instrumental.

For the empirical observation of the emission spectra of flames and explosions, the type of spectrograph employed is relatively unimportant provided the instrument covers the whole region of the spectrum which is likely to be of interest. The

usual types of small and medium-size quartz instruments give quite satisfactory results. In general, large resolving power or high dispersion tends to stress the importance of spectra with discrete fine structure, while continua or diffuse bands with unresolved fine structure are more noticeable on instruments of low resolving power, or if a wide slit is used. Observations of the emission spectra encountered in combustion processes are, however, seldom much affected by the type of spectrograph employed. In making a detailed analysis of a spectrum it is, of course, essential to have adequate resolving power and reliable measurements. Some hints on the instrumental limitations and precautions necessary to identify molecular spectra are given in the book by Pearse and the author ¹⁹⁵. For absorption spectra the limitations imposed by the instruments are more severe and are discussed in the appropriate section.

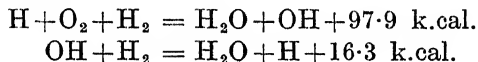
CHAPTER III

THE HYDROGEN FLAME

The OH Bands.

THE spectrum of the flame of burning hydrogen shows chiefly the strong band-system which is known to be due to the radical OH. A reproduction of the spectrum of an ordinary hydrogen-air flame is shown in Plate 1a. The strongest band is the (0, 0) band which shows an outstanding head, the R₂ head, at 3063.6 Å., this being accompanied by a second, R₁, head at 3067.2 Å. The Q₁ head at 3089 Å. usually shows up clearly, but the Q₂ head at 3078 Å. is less obvious. There are outstanding heads of weaker sequences of bands at 3428 (0, 1), 2811 (1, 0) and 2608 Å. (2, 0). The bands are degraded to the red and show a fairly open rotational structure, from the analysis of which it was shown by Watson²⁴⁴ and Jack^{129 130} that the emitter must be the diatomic hydride of oxygen, OH.

The knowledge that OH radicals were present in the flame led Bonhoeffer and Haber²⁷ to postulate a chain mechanism for the combustion of hydrogen of the type

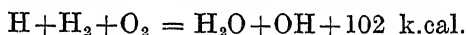


Several other chain mechanisms have been proposed for the reaction between hydrogen and oxygen, some involving radicals such as HO₂ and others being energy chains, but in practically all cases the production of OH radicals at some stage of the reaction, either as part of the main reaction chain or in some side chain, is presumed. The mechanism of the combustion of hydrogen has been discussed in the books by Kassel¹³⁹, Hinshelwood and Williamson¹²⁴ and Semenov²¹⁵, and in recent papers by Oldenberg and Sommers¹⁹² and Heiple and Lewis¹¹⁴.

The Low Pressure Flame.

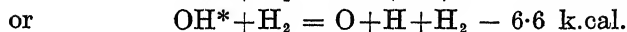
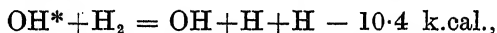
Kondratjew and Ziskin ¹⁵¹ have made quantitative measurements on the OH bands emitted by a flame of hydrogen burning in oxygen at pressures below 10 mm. of Hg. Measurements of the relative intensity of the (0, 0), (1, 0), and (2, 0) bands as occurring in this low temperature flame show that they are in the ratio of roughly 1 : 0.09 : 0.105, which is the same ratio as the calculated transition probabilities, and very different from the ratio of intensities calculated, assuming thermal equilibrium of the molecules in the vibrational levels of the upper electronic state. This is well shown in their microphotometer tracing of the spectrum in which the (2, 1) band is definitely stronger than the (1, 0) band, although a calculation of the relative intensities assuming thermal equilibrium at 1000° K., the approximate temperature of the flame, gives the ratio of the intensities of the (0, 0), (1, 0) and (2, 1) bands as 1 : 0.002 : 0.00007 and even at 2000° K. the (1, 0) band should still be 200 times as strong as the (2, 1). From this they conclude that the OH radicals are produced in the excited state by chemiluminescence and are not excited by thermal processes.

Kondratjew and Ziskin are thereby led to support the chain mechanism proposed by Bonhoeffer and Haber,



Allowing for the temperature of the flame (1000° K.) the available energy is then 110.5 k.cal. Excitation to the $v' = 0, 1, 2$ and 3 levels of electronically excited OH requires energies of 92.1, 100.5, 108.5 and 116.0 k.cal., respectively. Thus the OH radicals may be formed in the electronically excited state by the reaction process given above. A sudden falling off in the intensity of the (3, 2) band relative to the (1, 0) and (2, 1) bands, which is clearly seen in the microphotometer tracing, is accounted for by the reaction energy being insufficient to excite the $v' = 3$ level. It may be noted that the ordinary flame at atmospheric pressure does not show this remarkable falling off in the intensity of the (3, 2) band, which is clearly visible on the author's plate of the hydrogen flame (Plate 1a); this may be accounted for by the higher temperature of the normal flame, but may also indicate that the reaction processes are not necessarily quantitatively the same at higher pressure.

The presence of electronically excited OH radicals in the flame may result in chain branching by either of the mechanisms



These mechanisms, which have been discussed by Farkas⁷² and Herzberg¹²³, require small activation energies, as may be seen, but the temperature of the flame should be adequate to provide this energy.

Kondratjew and Ziskin have also made measurements on the total energy radiated from their low-pressure flames in the ultra-violet region of the spectrum, and find that the energy radiated corresponds to one quantum of OH radiation being emitted for about every 10^6 normal water molecules formed in the flame. These measurements, combined with the knowledge that the radiative life of the excited OH radical is of the order 10^{-6} sec. (see page 104), leads the author to conclude that the production of excited OH radicals by the Haber mechanism, while undoubtedly occurring to some extent, is a comparatively rare event under the conditions of Kondratjew and Ziskin's experiments; the radicals probably suffer not more than 10^8 collisions per second, so that even assuming that deactivation by collision was perfectly efficient, only one excited OH radical can be formed for about 1000 H_2O molecules ultimately produced.

The Continuous Background, etc.

In addition to the OH bands which dominate the spectrum, the hydrogen flame also shows a faint continuous background, chiefly in the visible region. Kondratjew and Ziskin¹⁵¹ suggested that this might be associated with the oxygen afterglow, which appears in the afterglow of water (Lavin and Stewart^{161 162}) when oxygen is present. The hydrogen flame is of course highly ionised, and these ions are mostly due to impurities rather than to ionised hydrogen, oxygen or water, and the yellow sodium lines and the near infra-red potassium lines are invariably present to some extent in the spectrum of the hydrogen flame. The deliberate introduction of an alkali metal into a hydrogen flame is known, and has been confirmed by the author, to produce a very strong continuum in the visible and near ultra-violet. Thus it seems that the faint continuum usually observed in the

spectrum of the hydrogen flame may be due, not to the oxygen afterglow, but to the presence of easily ionised impurities such as traces of sodium, potassium or calcium.

Kitagawa ¹⁴⁴ has observed a complex system of bands in the orange and red region when studying the spectrum of a flame of oxygen burning in hydrogen, and has tentatively identified these bands with the vibration-rotation spectrum of water. The confirmation of the presence of such highly activated water molecules in the flame would be of considerable interest.*

Candoluminescence.

The hydrogen flame, and to a less extent certain other flames containing hydrogen such as town's gas, possess the curious property of inducing luminescence in certain solids placed in contact with the flame. This phenomenon is now usually referred to as candoluminescence. It was first reported qualitatively in 1842 by W. H. Balmain and the importance of the phenomenon was stressed by J. Donau in 1913. Until recently most of our knowledge of the subject has depended on the researches of E. L. Nichols and colleagues at Cornell. Recently Smith ²²⁰ has published an interesting review of the subject and described certain experiments to check Nichols' work, and Minchin ¹⁷⁹ has given a demonstration of the effect.

The amount of light emitted by certain substances when heated to incandescence in a flame was stated by Nichols to exceed that emitted by a black body at the same temperature. Smith's experiments, however, indicate that this apparent effect is largely due to the incandescent surface being much hotter than the surface of a black body placed in the flame, and it seems that the peculiar variation of light emission with temperature may be due to variation of the thermal conductivity and emissivity with temperature. It therefore appears that the case for true candoluminescence at high temperatures is not proved, the bulk of the radiation being probably of thermal origin.

The candoluminescence exhibited by certain solids at temperatures below red heat is, however, undoubtedly a true

* Spectrograms of an ordinary oxy-hydrogen flame recently taken by the author using a large-aperture spectrograph show the bands in the red observed by Kitagawa. There are also additional bands in the photographic infra-red, including a strong band near 8100 Å.

luminescence. Many substances show marked luminescence when introduced into a hydrogen flame, boron nitride and calcium oxide activated with small amounts of bismuth, manganese, praeosodymium, etc., being favourite substances for demonstration of the effect. According to Smith, pure substances do not show the effect, the presence of an activator being essential, concentrations of activator of the order 1% giving the candoluminescence most strongly.

The spectra of such candoluminescent solids show regions of continuous emission, except in the case of praeosodymium as activator when a few lines are observed as well as a strong region of continuous emission. The spectrum appears to be determined by the activator rather than by the main substance, and the candoluminescence spectrum is generally very similar to the fluorescence spectrum of the same substance excited by ultra-violet light, although all candoluminescent substances do not appear to show fluorescence, and the optimum concentration of activator is much greater for candoluminescence than for fluorescence.

The cause of the phenomenon is still uncertain. There appear to be at least three possibilities, (i) that it is due to fluorescence excited by ultra-violet light from the flame, (ii) that the energy of certain activated molecules or atoms in the flame is passed on to the crystal lattice of the solid (active nitrogen has been observed to excite certain solids to luminescence) or (iii) the energy may be obtained by chemical reaction, such as alternate oxidation and reduction processes, induced catalytically at the surface. The present evidence seems to favour the second possibility, but final conclusions must await further experimental work. The phenomenon appears to be peculiar to the hydrogen flame, and its elucidation may be of interest for the theory of the combustion of hydrogen as well as being potentially important for the more efficient production of light from flames.

CHAPTER IV

HYDROCARBON FLAMES

IN this chapter it is proposed to describe and discuss the spectra, under various flame conditions, produced in the combustion of various hydrocarbons and related compounds, such as ethers and alcohols, which give spectra of similar type.

Using the usual Bunsen-type flame, it will at once be observed that the appearance of the flame, and therefore its spectrum, varies with the air supply, governed in the case of the Bunsen burner by the air hole at the base. With the air hole closed, a bright luminous flame is obtained. The spectrum of this shows chiefly continuous emission due to thermal radiation from carbon aggregates. With slightly increased air supply the flame becomes what is usually termed non-luminous, the bright yellow flame being replaced by a much less luminous transparent blue-violet flame. On further increasing the air supply the flame splits into two cones, the inner cone being bright blue-green, while the outer cone is less intense, being of a blue-violet shade. With still more air the inner cone changes back to a more violet shade of blue, but this condition is not usually reached with an ordinary Bunsen, a forced air draught being necessary.

The Inner Cone.

The inner cone of the Bunsen-type flame of burning hydrocarbons such as methane, ethylene, acetylene, and higher hydrocarbons and ethers, shows a rather striking banded spectrum, which is reproduced in Plate 1*d*. In the visible region the most prominent feature is the system of bands in the green, due to C_2 , which was first mapped by Swan in 1857 and is usually known by his name. In the violet at about 4315 and 3900 Å. there are strong bands of open rotational structure which are due to the radical CH; there are also a few weaker bands due to this emitter, including a band at 3143 Å. which only appears in relatively hot flames such as that of acetylene. The OH bands,

which have already been described, form the strongest feature of the spectrum in the ultra-violet, but there is also a weak system of bands of a more extensive character in the near ultra-violet. These weaker bands were first studied in detail by Vaidya ²³⁶, using an ethylene flame and have usually been referred to as the ethylene flame bands, but they occur in the spectra of the flames of all hydrocarbons and are referred to by Vaidya in later papers as the *hydrocarbon flame bands*, a name which will be used here.

With a not too copious air supply the Swan bands are the strongest feature of the spectrum of the inner cone, but the CH bands are also strong, with the hydrocarbon flame bands of moderate strength. With excess air the Swan bands are less pronounced, the change in the colour of the inner cone from blue-green to blue-violet being due to the weakening of the Swan bands. The CH bands remain strong, and the hydrocarbon flame bands are also still of moderate strength in the highly aerated flame. Some of the author's observations, using a sharply focused image of the flame on the slit of the spectrograph, indicate that the hydrocarbon flame bands may be produced a little lower in the flame than the bands of CH and OH.

In very hot flames, such as that of acetylene, weak bands due to CN and NH, and the γ bands of NO are sometimes observed.

The Outer Cone.

The spectrum of the outer cone of an ordinary Bunsen consists of the OH bands and the carbon monoxide flame spectrum ; a separate chapter is devoted to the discussion of the latter. The OH bands have already been described, but it is of interest to note that the appearance of these bands is rather different in the spectrum of hydrocarbon or coal-gas flames from that in the pure hydrogen-air flame. In hydrocarbon flames the heads of the bands are less outstanding, the structure of the bands stretches further to the red, and the (0, 1) band at 3428 Å. is seldom obvious in such flames, although it stands out clearly in the hydrogen flame. The relative intensity of the (0, 0) and (0, 1) bands should be constant in emission as it depends only on the transition probability and not on population, since the initial level is the same. The reason may be that for the hydrogen flame the heads stand out more clearly, so that the (0, 1) head is seen more easily above the background of the structure of the stronger

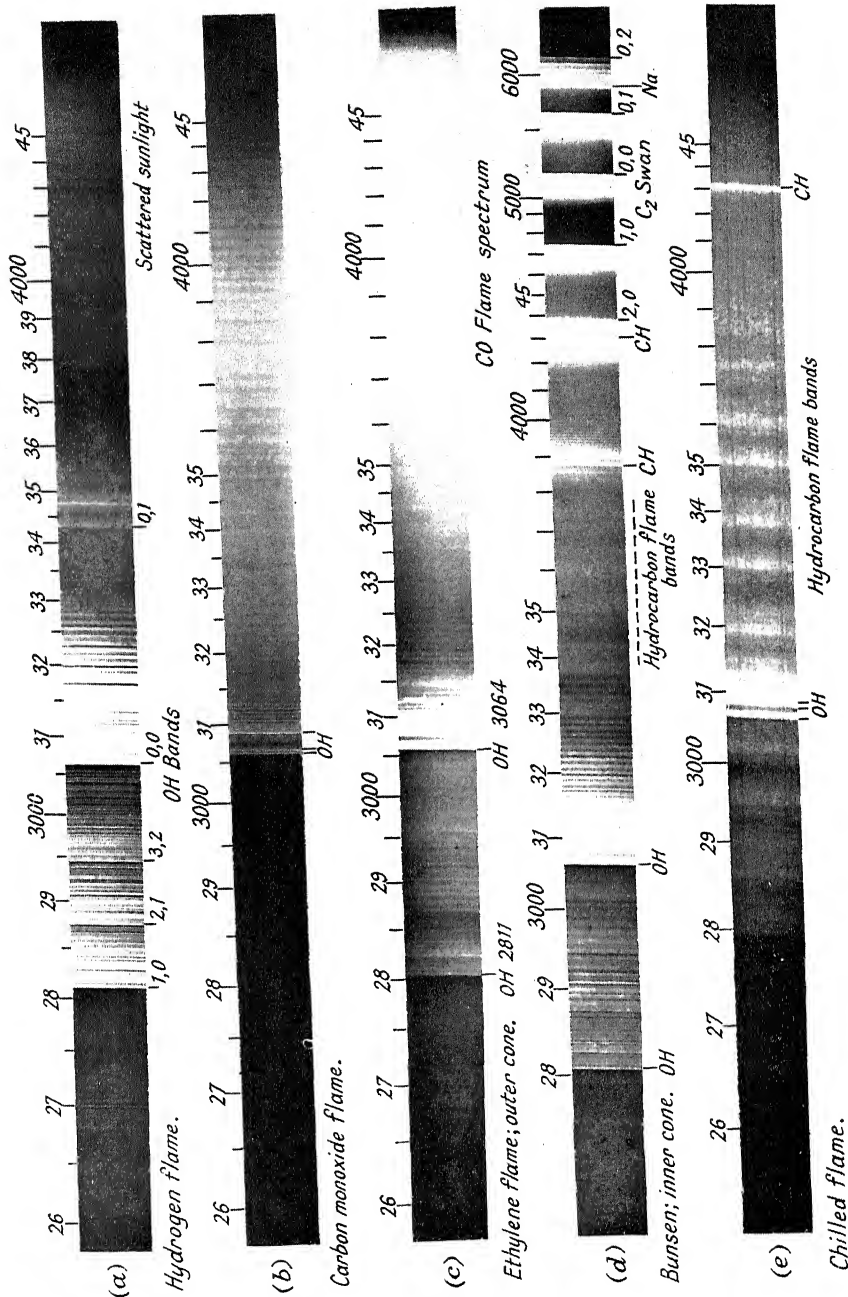
bands of the (0, 0) sequence. The reason why the heads stand out more clearly is not, however, obvious; it appears to be a temperature effect, the bands in hydrocarbon flames apparently having a higher effective rotational temperature than in the hydrogen flame, although the hydrogen flame should, according to actual measurements or calculations, be at least as hot as the flames of coal-gas or methane. It is difficult to express an opinion on the cause of the difference in the OH bands in the two flames without a quantitative knowledge of the effect and the factors involved, such as flame temperature, but this subject might be worth a more detailed study than it has so far received.

A reproduction of a rather heavily exposed spectrum of the outer cone of an ethylene flame is shown in Plate 1c.

The just non-luminous type of flame which is obtained with restricted air supply is really a blend of the inner and outer cones, the spectrum showing chiefly the OH bands, with the carbon monoxide flame spectrum and the CH and Swan bands present in fair strength. The Swan bands do not usually occur in the true outer cone, but the CH bands and hydrocarbon flame bands may show up under some conditions, especially if the inner cone is chilled.

Chilled Hydrocarbon Flames.

The author⁹² has recently made some observations on "struck-back" flames of burning coal-gas and hydrocarbons. The burner consisted of two concentric steel tubes about $\frac{1}{2}$ in. and $\frac{1}{8}$ in. internal bore, and about 3 ft. long. The inner tube was arranged so that it could be slid in and out of the outer tube, and was, in use, drawn back some 18 in. inside the larger tube. The inner tube was held centrally in position by three steel pins. The outer tube had an air inlet near the end through which the smaller tube was introduced, and was water-cooled over most of its length. A diagram of this very simple burner is shown in Fig. 5. A mixture of the combustible gas and primary air was introduced at the end of the inner tube, and a fast stream of secondary air was injected into the side tube. To strike the flame back it was usually necessary to thrust the inner tube forward, and then to draw it back gently to the required position. With suitable adjustment of air and gas supplies the inner cone rested on the tip of the inner tube, as indicated by the shading in



the diagram, and a long thin streak of flame at the end of the outer tube represented the outer cone.

The appearance of the flame under the various conditions of air supply was rather interesting. With a ratio of primary to secondary air of about 1 to 3, and with a very small total air supply, the inner cone consisted of a short blue-violet flame, and the outer cone appeared as a blue flame with a luminous tip. With slightly increased total air supply the inner cone became more blue-green in colour, and the outer cone became non-luminous, consisting of an ordinary transparent blue-violet flame which could easily be blown out. With a moderate air supply the outer cone blew out and could not be re-lit. With a still faster flow of air, however, a long blue streak of flame reappeared at the end of the outer tube; this streak could not be blown out and was of a different character from the flame of the outer cone

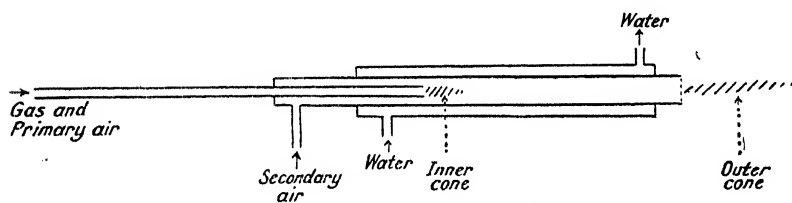


FIG. 5.—Burner for chilled flames.

obtained with a small total air supply. With even faster air flow the blue streak shrunk back into the tube, and finally disappeared; the inner cone was less bright and of a more blue-violet shade under these conditions of very fast air flow.

The most interesting condition of the flame was the blue streak of light corresponding to the outer cone which was observed with a fairly fast stream of air. This only appeared over a rather narrow range of air supply, this range becoming narrower as the inner tube was drawn back further so that the separation between the inner and outer cones was increased, and finally when the inner tube was drawn in some 22 to 24 in. the blue streak disappeared altogether. Conversely, when the inner tube was thrust forward the blue streak became brighter and was present over a wider range of total air supply, and finally, when the separation between the inner and outer cones was reduced to about 12 in., the blue streak merged with the non-luminous

flame obtained with restricted air supply, and there was little distinction between the two conditions of the flame, except that for small air flow the outer cone could be blown out, while with a faster flow it could not.

With an increased ratio of primary to secondary air supply the inner cone of the flame became luminous and even smoky, but the same general effects were observed. In this case the blue streak appeared as rather jagged tongues of blue light surrounding a thin luminous flame which was really an extension of the tip of the inner cone.

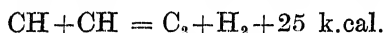
The blue streak was remarkable in that, under suitable conditions, its spectrum showed as its strongest feature the hydrocarbon flame bands. The OH band and the CH band at 4315 Å. were usually present, and in some cases the carbon monoxide flame spectrum made its appearance. The plate shown (Plate 1e) is a reproduction of the spectrum of this blue streak for a town's gas flame using a fairly fine slit. Some of the plates, taken with a wide slit on a weaker flame when the inner tube was drawn back farther, and on a flame of pure ethylene, show the hydrocarbon flame bands more strongly relatively to OH and CH, and some of these are reproduced in the original paper. Similar results were obtained with town's gas, ethylene, methane, butane and acetylene, and the spectrum and flame conditions were not affected appreciably by the introduction of such catalysts as ethyl nitrate (promoter) or propyl bromide (inhibitor). For further details on the spectrum and appearance of this chilled flame the reader is referred to the original paper. It will suffice here to say that the hydrocarbon flame bands appear strongly in the outer cones of flames when the inner cone is chilled, the bands being much more clearly developed when the outer tube was water-cooled than when it was allowed to become heated. Chemical tests showing the relation between the flame bands and the occurrence of peroxidic substances in the chilled flame are described later, when the origin of the bands is dealt with.

The Swan Bands.

The Swan bands form a compact system in the green region of the spectrum. The bands are degraded to the violet and show well-marked sequences, the (1, 0), (0, 0) and (0, 1) sequences having outstanding heads at 4737.1, 5165.2 and 5635.5 Å.

respectively. A full list of the bands of this system is given in the appendix and the system is shown in Plate 1*d*. The emitter of the Swan bands was for long in doubt, the system being variously attributed to carbon or to a compound of carbon with oxygen or hydrogen. The study of the rotational structure of the bands, revealing alternating intensities, which are known to be characteristic of homonuclear molecules, and experimental work by Pretty²⁰¹ finally established that the emitter was diatomic carbon, C₂.

The cause of the strong emission of the Swan spectrum from hydrocarbon flames is uncertain. It is usually assumed that the carbon is formed by thermal decomposition (cracking) of the hydrocarbon, but observations by Smith²¹⁹ (see page 66) on carbon deposition and the occurrence of the Swan bands in explosions of propane and ethylene with oxygen throw some doubt on this. Also a thermal decomposition theory has difficulty in explaining the presence of the C₂ bands in the spectrum of the flame of methane, in which they occur nearly as strongly as they do in the flames of the higher saturated hydrocarbons; C₂ molecules cannot, of course, be produced by simple collision of two carbon atoms, and a three-body collision might be expected to leave the carbon combined in some other form. The C₂ molecules might be formed by collision of two CH radicals,



a reaction which is strongly exothermic, but does not give sufficient energy for the electronic excitation of the C₂ molecules produced.

The CH bands.

The strongest CH band at 4315 Å. corresponds to a ²Δ to ²Π transition, the lower state being presumably the ground state for CH. The Q branches form a strong head at 4312.5 Å. and a weaker head at 4315 Å., while the lines of the P branches close up to form what appears, under moderate dispersion, to be a head at about 4384 Å. A weak (0, 1) band of this system is known at around 4890 Å. and may show heads at 4942, 4937 and 4890 Å.

The 3900 Å. band, which is also quite strong in hydrocarbon flames, is due to a ²Σ → ²Π transition, the final state being again the ground level. The rotational fine structure of this band shows

up rather more clearly than does that of the 4315 band. The band is degraded to the red and forms an R head at 3872 Å. and a Q head of comparable strength at 3889 Å. Weak (1, 1) and (1, 0) bands of this system with Q heads at 4025.3 and 3628 Å. respectively are sometimes observed on heavily exposed spectrograms.

The band at 3143 Å. is also due to a $^2\Sigma \rightarrow ^2\Pi$ transition, the final $^2\Pi$ level being again the ground one. This band is not strongly degraded either way, so that the Q branches form a strong maximum at 3144 Å. Under moderate or small dispersion this maximum may easily be mistaken for an atomic line, and is usually partly obscured by the OH band. The band does not appear strongly in the flames of town's gas or methane burning in air, but comes up more clearly in hotter flames such as that of acetylene, and in the flames of methane and higher hydrocarbons burning in oxygen.

The fact that all three systems of CH are present in flames, and that the system with the lowest excitation energy is the strongest, and that the 3143 band which requires a rather higher excitation energy than the others only appears in the hotter flames, suggests that the spectrum of CH is excited thermally rather than by chemiluminescence. In view of the strength of the CH bands this might lead us to assume that the CH radicals were very abundant in flames. This, however, appears at variance with the fact that, as far as the author is aware, the CH bands have never been observed in absorption by flame gases. Two possible explanations present themselves. The first is that the $^2\Pi$ level is not in reality the ground state of CH; the Wigner-Witmer correlation rules predict a $^2\Pi$ level as the ground state for CH, but they also predict a $^4\Sigma$ level of low energy; this $^4\Sigma$ level has not been observed, probably because transitions to it from the other doublet levels would be negligibly weak on account of the change of multiplicity, but it is conceivable, although unlikely, that it may lie below the $^2\Pi$ level. The second possible explanation is that the strength of the bands relative to those of other emitters is due not so much to the high concentration of CH radicals as to their long collision life, which would give them a much better chance of radiating (see page 23 *et seq.*). It has indeed been suggested by Smith²¹⁹, in discussing the flame spectrum of ethylene, that the persistence

of CH bands throughout the entire range, except for mixtures very rich in ethylene, is in accord with the theoretical expectation that these molecules, being in a ${}^2\Pi$ state, would not readily react with oxygen molecules in the lowest ${}^3\Sigma$ state. The same considerations should perhaps apply to CH molecules in the excited ${}^2\Pi$ and ${}^2\Sigma$ states and to their reaction with other molecules present such as C_2 , N_2 , H_2O , CO_2 , all of which have an odd multiplicity, only OH of the relatively abundant molecules present having doublet terms. This may therefore account for the long collision life of the excited CH radicals and therefore for the apparently surprising strength of the CH bands in flame spectra.

The Hydrocarbon (or Ethylene) Flame Bands.

These bands were first studied in detail by Vaidya ²³⁶, who gave a very complete account of the appearance of the system, with an arrangement of the bands into a provisional vibrational scheme. The system lies in the region 2500 to 4000 Å., the bands being strongest in the region between the intense OH and CH bands which usually accompany them. The hydrocarbon flame bands are degraded to the red and show fairly well defined heads, of which Vaidya records the wave-lengths and intensities of some three dozen. The heads at 3588.6, 3502.7, 3377.4, 3299.2 and 3014.8 are strong and fairly free from overlapping by the OH or CH bands and therefore serve to identify the system.

Vaidya observed the bands in an ethylene-air flame, several types of burner being used, including a Smithell's flame separator, in which the bands were observed in the inner cone, a two-way blowpipe, and a special multiple capillary jet burner which is fully described in the original paper. The appearance of the band system was found to vary considerably according to the type of burner employed, and Vaidya classified the bands into two groups, which he designated as *A* and *B*, according to whether they appeared relatively more strongly in the ordinary separated flame or in the multiple jet flame.

Some 22 of the bands of Group *A* can be arranged quite satisfactorily into a vibrational scheme similar to that of Table 2 (page 8), using differences of 1876 cm^{-1} decreasing by steps of about 23 cm^{-1} , and 1066 decreasing by about 12 cm^{-1} , so that the values of the vibrational frequencies ω' and ω'' will have values of about 1072 and 1960 cm^{-1} , the value for the

latter being rather uncertain, the actual value depending on the assignment of the values of the vibrational quantum number ν'' which cannot be fixed definitely from the vibrational scheme. Other weak bands of Group *A* form short progressions using the same value of ω'' , and all but one of the *B* bands fall into two progressions separated by intervals of about 240 and 154 cm^{-1} from the two strongest progressions of the *A* group.

This separation of the bands into two groups, although justified by the analysis, does not appear very striking to the author, who has found little evidence for it on his plates, and does not find the classification very obvious from Vaidya's published photographs. It seems likely that the *A* and *B* bands are in reality different heads of the same bands, the temperature of the flame affecting the relative strength of these heads in much the same way as the appearance of the OH bands is different in some flames from others.

These hydrocarbon flame bands occur relatively strongly in the inner cone of an ethylene flame, but are also well developed in the flames of acetylene, methane, propane, and higher hydrocarbons, of ethers, of benzene and other aromatic compounds ²³⁷ such as toluene, phenol, benzaldehyde, benzoic acid, pyrogallol, nitrobenzene, etc., ethyl alcohol, acetaldehyde, methyl chloride, chloroform and of mixtures of hydrogen and carbon tetrachloride ²⁴⁰. The bands are not, however, observed in the flames of formaldehyde or formic acid ^{237 106}, which show only the OH bands and carbon monoxide flame spectrum. Guénault ¹⁰⁶ states that the bands are present in the flame of methyl alcohol, which also shows the cool flame spectrum of ether, but Vaidya ²⁴⁰ did not detect the hydrocarbon flame bands in this source, although he observed the CH bands.

In addition to these observations of the bands in the inner cones of various flames, it has already been pointed out that they occur in the outer cones of chilled hydrocarbon flames (Gaydon ⁹²), in which source they are relatively much stronger compared with the bands of CH and OH. See Plate 1e.

The Emitter of the Hydrocarbon Flame Bands.

Although many of the hydrocarbon flame bands can be arranged into a single vibrational scheme similar to that for a diatomic molecule, a few bands definitely do not fall into the

scheme, and require separate arrays. This shows that either more than one system of bands is involved, which, from their appearance, seems very unlikely, or that more than a single series of vibrational levels in each electronic state is required to represent the bands; this would mean, of course, that the emitter is not diatomic. This conclusion is supported by the absence of any agreement of the vibrational frequencies with those known for the diatomic molecules which are present in the flame (OH, CH, C₂, O₂, CO). The bands do not show any agreement with the known ultra-violet absorption or fluorescence spectra of formaldehyde. Vaidya was thus led, on the suggestion of the late Professor Fowler, to attribute the bands to the molecule HCO. Vaidya supports this hypothesis by comparing the band system with that of the isoelectronic molecule NO, the well-known β system of which lies in the same region of the spectrum as the hydrocarbon flame bands and has vibrational frequencies of 1029 and 1889 compared with the observed values of 1072 and about 1960 for the flame bands.

Vaidya suggested that the HCO radicals might be formed by the direct introduction of an oxygen molecule into the ethylene molecule, which could then decompose to give two HCO radicals and molecular hydrogen.

Bell¹⁸, who studied the flame spectra of methane, methyl alcohol and formaldehyde, tentatively attributed the bands to the radical CH₂, favouring this in preference to HCO, because, on the hydroxylation theory of hydrocarbon combustion, it seemed reasonable to expect that CH₂ radicals might be formed by the thermal decomposition of methyl alcohol produced during the early stages of the combustion process. All other observations, however, indicate that oxygen is essential for the production of the hydrocarbon flame bands, and recent photographs of the spectrum taken by the author using a large Littrow type (Hilger E.1) quartz spectrograph show clearly that the rotational structure of the bands is so close that the emitter must have a moment of inertia much higher than could be obtained from CH₂, which is therefore definitely ruled out.

The experiments of Smith²¹⁹ on the conditions of the occurrence of the hydrocarbon flame bands and other spectra in stationary and explosion flames made him conclude that the emitter was a molecule containing oxygen, and the usual close

association of the flame bands with the systems of CH and OH led him to suggest that the emitter might be an isomeric formaldehyde molecule HC.OH; this would, he says, provide a possible explanation for the observed increase in the production of formaldehyde in the combustion of mixtures containing a large excess of oxygen.

Perhaps the most definite chemical tests relating to the production of the hydrocarbon flame bands are those on the interconal gases of chilled hydrocarbon flames⁹², the spectrum of the outer cones of such flames showing the flame bands relatively free from other band systems. In this case chemical sampling showed that the interconal gases contained large amounts of both formaldehyde and peroxidic substances; the testing solutions were turned acid, probably by the formation of formic and similar acids, but no acetylene or nitrogen peroxide was detected. It was shown conclusively that the presence of the hydrocarbon flame bands in the outer cone was always associated with the formation of peroxidic substances in the interconal gases, and that although aldehydes, mostly formaldehyde, were usually present as well, the strength of the aldehyde formation did not follow the strength of the flame bands in the spectrum, but the formation of peroxides did correspond closely with the strength of the flame bands. The tests for peroxides were carried out by bubbling the gases through distilled water for a known time, usually ten minutes, and then testing with potassium iodide acidified with dilute acetic acid. When burning methane or town's gas, it was found that the test for peroxides was very sensitive to the pH of the testing solution, the test being, under suitable flame conditions, strongly positive when the distilled water was made slightly alkaline, but with a slightly acid testing solution very little peroxide was collected. Using an initially nearly neutral solution, the collection of acids from the interconal gases resulted in the sample being slightly acid by the time it was tested with potassium iodide, so that the peroxide was recorded without the need of adding acetic acid as well, but if the sample was carefully neutralised before adding the iodide only a little iodine was liberated, but the addition of acid resulted in the slow liberation of a considerable amount of iodine. This seems to indicate that although a little per-acid was present, the bulk of the peroxide was present in the form of an alkyl peroxide.

When burning ethylene the test for peroxides was less dependent on the pH of the sampling solution, but strong liberation of iodine was again only obtained when the potassium iodide was acidified, and even then came up rather slowly; thus it seems that the peroxide formed from ethylene was not the same as that formed from methane, but was also probably of an alkyl type.

These chemical tests led the author to support Vaidya in assigning the bands to HCO . It is suggested that these radicals might be formed in the decomposition of alkyl peroxides in much the same way as CH radicals are known, from spectroscopic evidence, to be formed in the decomposition of hydrocarbons, either on combustion or in electric discharges. Thus, Professor Egerton suggested that for methane, the first step in the combustion might be the formation of a complex, $CH_4 \cdot O_2$, which might then either stabilise into the alkyl peroxide CH_3OOH or decompose into $HCO + OH + H_2$.

Two other possible emitters which might be postulated are CHO_2 and $C \cdot OH$. The former might be produced in the breaking up of peroxides, but the breaking up would be less simple than that suggested above to account for the production of HCO radicals, or alternatively it might be produced by the union of CH with oxygen. The $C \cdot OH$ radical might be favoured by supporters of the hydroxylation theory, but the correspondence between the occurrence of the bands in the chilled flames and peroxide formation seems against the hypothesis that $C \cdot OH$ is the emitter. The isomeric formaldehyde molecule, which Smith suggested might be the emitter, would probably require a three-body collision for its formation from CH and OH , and this collision might be expected to stabilise the new molecule to formaldehyde itself. Also the bands have not, as far as the author is aware, been observed in discharge tubes even though OH and CH bands may be present together in such sources; the failure to observe the bands in discharge tubes might be due to the lower pressure of the discharge, but does nevertheless suggest that the emitters of the flame bands are formed during the combustion process rather than by collisions of OH and CH . Perhaps the hardest test of all these hypotheses on the nature of the emitter is the observation by Vaidya²⁴⁰ of the flame bands in mixtures of hydrogen and carbon tetrachloride burning in air, an observation which does not seem to be explained at all readily.

Study of the flame bands under high dispersion reveals that the bands possess a fairly close rotational structure consistent with the molecule having a moment of inertia of the same order as that for CO, NO, and like molecules, and there does not appear to be any larger scale structure to the bands suggestive of a smaller moment of inertia. Thus if the emitter is either HCO, HC.OH or C.OH it must be linear, or very nearly so, as otherwise the spectrum should show a smaller moment of inertia due to rotation about the C—O axis. With this reservation both the rotational and vibrational structure of the bands would agree with the bands being emitted by any of the above-mentioned molecules; these molecules should also show a vibrational frequency rather greater than that used for the vibrational scheme given by Vaidya, corresponding to the vibration of the lighter H atom relative to the heavier atoms, and this vibration might account for the bands which do not fit into the main array, but the bands observed are too few in number to permit of a determination of this frequency.

It is unfortunate that the emitter of a band system which is of such interest to the theory of combustion should be still in doubt, but at present there does not seem to be any crucial test which can be applied.* The association of the band system with the formation of alkyl peroxides leads the author to favour the radical HCO as the emitter.

The Mechanism of Hydrocarbon Combustion.

The mechanism of the initial stages of the combustion of hydrocarbons is a very controversial subject. The two main theories are usually referred to as the hydroxylation theory and the peroxidation theory, both theories having a number of possible variations.

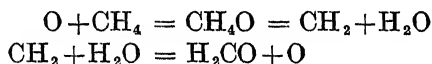
The original hydroxylation theory as put forward by the late Professor Bone maintained that the initial stages in the combustion were the successive introduction of OH groups into the hydrocarbon molecule, so that the oxidation of a hydrocarbon RCH_3 may be represented as



* Dr. Vaidya has recently informed the author that he has obtained the hydrocarbon flame bands from an atomic flame of deuterio-acetylene, and hopes to make use of the isotope effect in the bands to identify the emitter.

According to the peroxidation theory as suggested by Callendar and developed by Professor Egerton⁵³ and others, reaction occurs when a sufficiently energetic hydrocarbon molecule combines momentarily with an energetic oxygen molecule, forming a temporary peroxide in a high energy state. Among the changes which may then occur, breakdown to aldehyde and water is possible, and the energy carried by these molecules may then continue the combustion process.

These theories have been discussed, and variations have been suggested by Norrish¹⁸⁷, Bone and Gardner²², Ubbelohde²³¹ and von Elbe and Lewis²⁴³. Norrish modified the hydroxylation theory, so that the hydrocarbon is supposed to react with atomic oxygen to form, initially, a complex RCH_3O , which could stabilise to the alcohol at the surface or on suitable collision, but which would normally break down to the radical RCH and water, so that for methane the process was visualised as follows :

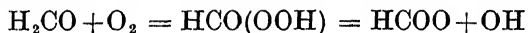


so that the chain was carried along alternately by CH_2 and O . The oxygen atoms were supposed to be formed initially at the surface by oxidation of aldehyde to a peroxide which then decomposed into acid and atomic oxygen

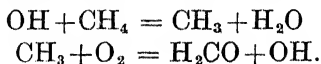


Ubbelohde starts from the aldehyde oxidation mechanism proposed by Bäckstrom and develops a number of rather complicated chain mechanisms for hydrocarbon oxidation, the chain being propagated by the radical RCH_2 and the peroxidic body RCH_2OO .

In von Elbe and Lewis's view the chains are propagated by hydroxyl and RCH_2 radicals, the OH radicals being formed initially at the walls by oxidation of aldehydes, so that for formaldehyde the reaction is initiated at the surface by



and the chain is continued, by methane, as follows :



Some of these theories will be referred to again in discussing the spectra of cool flames.

The empirical study of the emission spectra of hydrocarbon flames has made surprisingly little direct contribution to the theory of the combustion mechanism. The observation of free radicals in the spectra of flames has, of course, had a marked influence in the use of radicals in the various chain mechanisms, but it is disappointing, to a spectroscopist, to find that the very radicals which appear most strongly in the flame spectra, CH and C_2 , are not included in the combustion processes. It is, of course, assumed that these radicals are produced by thermal decomposition or perhaps by side reactions of the various radicals present, and considerations such as those discussed in Chapter II and on page 38 can no doubt be invoked to account for the strength of the emission spectra of C_2 and CH .

The hydrocarbon flame bands may have a greater bearing on the combustion theory, but it must be remembered that this is a weak band system, and if conclusions cannot safely be drawn from the presence of strong systems such as CH , still less may conclusions safely be drawn from a weak system, without a quantitative knowledge of the concentration of the emitters and details of its nature. The author's observations indicate that the flame bands are, in the spectra of chilled flames, associated with the presence of alkyl peroxides, and may therefore be taken as evidence in favour of a peroxidation rather than a hydroxylation theory, but give no definite indication of the best variant of the peroxidation theory.

Guénault ¹⁰⁶ states that the ordinary flame spectrum of methyl alcohol shows the band system first observed in the cool flame of ether. The flames of burning hydrocarbons do not show this cool flame spectrum, and Guénault interprets this as indicating that methyl alcohol is not therefore an intermediary in the combustion process.

The evidence for the existence of the methylene radical, CH_2 , has been discussed by Barrow, Pearson and Purcell ¹², who have referred to spectroscopic calculations of the structure and stability of this radical and also HCO . In a discussion of a paper presented at a meeting of the Faraday Society, Mecke ¹⁷⁶ said that he had observed weak absorption bands at 4370 and 4020 \AA . which were obtained during the thermal decomposition of methane, and he

suggested that these bands might be due to the radical CH_2 . These observations, which are obviously important, do not appear to have been confirmed and there seems little evidence to show that the bands are due to CH_2 rather than to CH_3 or some more complex compound.

CHAPTER V

COOL FLAMES AND ATOMIC FLAMES

Cool Flames.

MANY hydrocarbons and related compounds will react slowly with oxygen at temperatures well below the ignition temperature corresponding to the production of normal flame. In some cases this slow combustion may be accompanied by the emission of light in the form of either a faint glow of the reacting gases or a cool flame which slowly traverses the mixture. The cool flames only occur within rather narrow limits of temperature and pressure peculiar to the particular gases and mixture strength. Occasionally several, perhaps as many as five, cool flames may be seen to traverse the mixture, one after the other in fairly rapid succession. At temperatures above those favourable for the occurrence of the cool flames but still below the ignition temperature, the reacting mixture is usually found to glow, the brightness of this glow increasing as the ignition temperature is approached.

Chemical sampling of the products of the slow oxidation of hydrocarbons at various stages during the oxidation shows that a variety of compounds are produced, among which are alcohols, peroxides, aldehydes, acids, unsaturated hydrocarbons, etc. In all cases there appears to be a definite induction period before appreciable reaction, or the passage of the cool flame, occurs.

Cool flames have been observed for the higher hydrocarbons, aldehydes and ethers, but not for methane or formaldehyde. A number of inorganic compounds such as phosphorus and carbon disulphide also show luminescence when undergoing low-temperature oxidation, and these are discussed in the chapter on inorganic emission spectra. These cool flames and glows are of course feeble sources of light, and very long exposures are required to photograph their spectra even on instruments of the greatest light-gathering power, but Emeléus and colleagues have succeeded in

recording the principle features of the spectra of several of the most interesting of these flames.

The Cool Flame Spectrum of Ether.

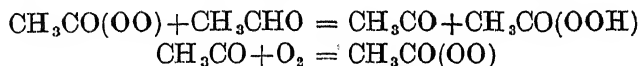
The cool flame of ether was first studied spectroscopically by Emeléus⁶¹, who obtained satisfactory plates with exposures of between 180 and 250 hours using a rather wide slit. The spectrum, a photograph of which is reproduced in Plate 2*a*, is quite different from that of the normal flame of ether, and consists of a number of bands, shaded to the red, which are strongest in the blue to near ultra-violet region of the spectrum. Owing to the rather wide slit the wave-lengths given by Emeléus were not very accurate, being actually systematically too low, and the emitter of the bands was unknown for some years. Kondratjew¹⁴⁵ suggested that the bands might be due to formaldehyde, and, following the recording of the fluorescence spectrum of this molecule by Herzberg and Franz^{123*a*}, it was shown by Pearse (see Ubbelohde²³¹) by direct comparison of spectrograms that the cool flame spectrum was indeed identical with the fluorescence spectrum of formaldehyde. This identity has also been checked by Kondratjew¹⁴⁷, who remeasured the centres instead of the edges of the bands of the cool flame obtained by Emeléus, thus eliminating the error in the wave-lengths due to the use of the wide slit.

Emeléus⁶³ has also examined the spectra of the cool flames of acetaldehyde, propaldehyde and hexane, and finds that all these are identical with the cool flame of ether. Thus all the cool flame spectra of this type are due to the same emitter, formaldehyde.

Combustion Processes in Cool Flames.

These cool flames occur at quite low temperatures, usually below 400° C. and sometimes below 200° C., so that the excitation of the formaldehyde molecules cannot occur thermally, but must be a chemiluminescent phenomenon. The combustion processes during the low-temperature reaction are probably rather different from those in ordinary flames and explosions, and the presence of activated formaldehyde molecules in the cool flame has naturally been taken into account in discussing the mechanism of the combustion.

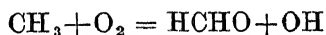
Von Elbe and Lewis²⁴³ have discussed the probable chain mechanism in the low-temperature oxidation of hydrocarbons and aldehydes on a modified peroxidation theory, and favour a mechanism in which CH_3CO radicals take part; thus for acet-aldehyde the oxidation mechanism takes the form:



but with some of the CH_3CO radicals being removed by the reaction



the reaction being accompanied by the evolution of about 110 k.cal., which is available for the formation of the activated formaldehyde molecules, HCHO^* , which give the observed luminescence or cool flame. This explanation appears satisfactory in that it explains the chemiluminescent excitation of the formaldehyde molecules in the slow combustion of the higher aldehydes and hydrocarbons, while, although formaldehyde is produced in the high temperature combustion, according to von Elbe and Lewis, by the reaction



which forms part of the chain mechanism for the oxidation of methane and higher hydrocarbons, the formaldehyde molecules so produced will not be excited and so do not give the formaldehyde emission spectrum, which is only given by the cool flame.

Atomic Flames.

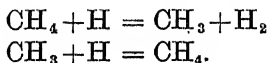
In addition to the cool flames observed in slow combustion, low-temperature flames are also produced when atomic oxygen or atomic hydrogen obtained from discharge tubes is mixed with hydrocarbon or other vapours. The apparatus for producing these atomic flames consists essentially of a discharge tube through which the oxygen or hydrogen is allowed to flow at reduced pressure (~ 1 mm. Hg), the gases from the discharge being pumped rapidly away so that they mix with a stream of the hydrocarbon or other vapour outside the discharge tube. In many cases an intense glow is produced where the gases mix.

Tests show that the gases from the discharge tube contain a

high proportion (as much as a quarter by volume) of free atoms. These free atoms have a comparatively long life in the gas phase and are thus able to persist until they meet the stream of hydrocarbon gas with which they react. The experiments are, of course, of interest in relation to the theory of combustion as in many cases chain mechanisms involving atomic oxygen or atomic hydrogen are proposed to explain reactions under ordinary flame conditions.

Atomic oxygen gives these so-called atomic flames with the higher hydrocarbons, and many other organic compounds including methyl alcohol and formaldehyde, but Harteck and Kopsch ¹⁰⁹ did not observe flames with methane, hydrogen or carbon monoxide, with all of which the reaction was very slight. The failure to observe appreciable reaction with methane must be regarded as very strong evidence against Norrish's modified hydroxylation theory ¹⁸⁷, in which the oxidation of methane is supposed to be maintained by a chain mechanism involving atomic oxygen.

The reactions of atomic hydrogen have been studied by Bonhoeffer and Harteck ²⁸. With methane there is again little reaction, the chief effect being recombination of the hydrogen atoms to form molecules, probably by the reactions,



With higher hydrocarbons the atomic hydrogen appears to be able to either hydrogenate unsaturated compounds by addition, or to dehydrogenate the hydrocarbon by removal of an atom of hydrogen to form molecular hydrogen.

The Spectra of Atomic Flames.

The spectra of these atomic flames differ very little from those of the inner cones of the corresponding ordinary flames. The spectra obtained from atomic flames with oxygen have been studied by Harteck and Kopsch ¹⁰⁹, Bonhoeffer ²⁶, and Geib and Vaidya ⁹⁵. For hydrocarbons, except methane, an intense greenish glow is observed which shows a spectrum very similar to that of the inner cone of an ordinary Bunsen, the principal features being the strong Swan bands of C_2 , the CH bands and the OH band at 3064 Å. The hydrocarbon (or ethylene) flame bands are also present, these being shown most strongly by

acetylene and benzene, in which both groups *A* and *B* appear. The hydrocarbon flame bands are relatively weak and diffuse in the atomic—oxygen—ethylene flame, although ethylene, of course, shows these bands most clearly in ordinary flames. Formaldehyde only shows OH bands in the atomic flame, as in the ordinary flame. Methyl alcohol shows strong OH, but also some CH and the formaldehyde emission similar to that of the cool flame of ether.

It thus seems, from the spectroscopic evidence, that the low-temperature flames produced by atomic oxygen are very similar in character to ordinary flames, and differ from the cool flames observed in slow combustion in which atomic oxygen cannot presumably play an important rôle.

Atomic flames produced by hydrogen have been studied by Bonhoeffer and Harteck²⁸. These flames show strong C_2 and CH bands. According to Geib and Vaidya, the atomic hydrogen-benzene flame does not show the hydrocarbon flame bands, which probably require oxygen for their production. As pointed out by Bonhoeffer and Harteck, and stressed by Hsieh and Townend¹²⁶, collisions of hydrogen atoms with hydrocarbons higher than methane may successively strip off the hydrogens of the hydrocarbon so that ultimately CH and finally C_2 radicals predominate. This may account for the strong production of C_2 and CH radicals in flames, which otherwise does not seem to fit easily into the ordinary combustion theories. The hydrogen atoms might, for instance, be produced to some extent by the combustion of hydrogen (see page 27) and then react with the hydrocarbon to form CH and C_2 . A more elaborate mechanism would, however, be required to account for the appearance of CH or C_2 bands in the spectrum of the ordinary flame of methane, which gas is almost unaffected by atomic hydrogen or oxygen.

CHAPTER VI

THE CARBON MONOXIDE FLAME

The Spectrum.

THE spectrum of the flame of carbon monoxide burning in air or oxygen consists of a faint banded spectrum superposed on a strong continuous background which extends throughout the visible and near ultra-violet, being strongest in the region 4500 to 3500 Å. Unless great precautions are taken to dry the gases, the OH band at 3064 Å. is invariably present in the spectrum of the flame. If the carbon monoxide is stored in steel cylinders a little iron carbonyl is formed and this is carried into the flame, which may then show iron lines and iron oxide bands in its spectrum; the iron carbonyl can be eliminated from the flame by passing the carbon monoxide through a heated tube packed with crushed porcelain. The spectrum has been studied and discussed by Weston ²⁴⁶ ²⁴⁷, Kondratjew ¹⁴⁵ and the author ⁸⁹ and a reproduction of a spectrogram is shown in Plate 1b.

The spectrum has most frequently been photographed on instruments of moderate dispersion, using fast photographic plates of low contrast, and with the flame burning at atmospheric pressure. Under these conditions the band system does not show up at all clearly above the continuous background. If, however, a reduced pressure flame is used the band system appears to be relatively more prominent, and Kondratjew used this method to make his measurements of the bands. There is also a marked difference in the appearance of the spectrum when recorded on plates of very high contrast, such as half-tone plates, and these were used by the author, and were found to resolve into two or more components many bands previously recorded as single, and to enable more precise measurements to be made.

As will be seen from the plate, the spectrum consists of a very large number of narrow headless bands superposed on the continuous background. Many of the bands appear to be

arranged in pairs, as has been remarked by Kondratjew. Some of the bands, especially those at the red end of the spectrum, show signs of being degraded to the violet, while a few appear to be shaded in the other direction. This degradation of the bands is not, however, striking and may be due to overlapping of bands of different intensities producing this effect. Many of the bands at the shorter wave-length end of the spectrum show signs of rotational fine structure. This fine structure appears more clearly under higher dispersion, and Kondratjew has expressed the opinion that the continuous background may in reality be composed of numerous fine lines due to the rotational fine structure of the spectrum.

The Structure of the Band Spectrum.

The band spectrum is very complex and, apart from the arrangement of many of the bands in pairs, shows no obvious regularity. The system is far too complex for a diatomic emitter, and we must therefore expect to find more than the two fundamental frequency differences characteristic of the band system of a diatomic molecule. The difficulty of the analysis is very much increased by the diffuseness of the bands, which prevents one from obtaining accurate measurements.

The first attempt at an analysis of the spectrum was made by the late Professor Fowler and is included in Weston's first paper. Many of the strongest bands were arranged by Fowler into arrays, using intervals of around 570 and 370 cm^{-1} . Kondratjew arranged the bands in long series with intervals increasing from around 550 cm^{-1} to over 600 cm^{-1} , this interval being provisionally identified with the interval of 667 cm^{-1} observed for the infra-red spectrum of CO_2 . These long series were not, however, completely confirmed by the author's measurements, the intervals and intensities showing disturbing irregularities in some cases.

With such a complex spectrum, consisting of diffuse bands every few angstroms, great care must be taken not to force the analysis to fit any preconceived ideas. To avoid this difficulty the author adopted an approximately statistical approach to the analysis. Using the measurements of all the strong bands, all the wave-number differences between these bands were computed up to a difference of 2400 cm^{-1} , this presumably covering

the range of any vibrational frequencies likely to be encountered. The number of differences in successive equal intervals was then counted up, and these numbers were then plotted against the mean differences. This should show up at once any regularity in the spectrum, as wave-number differences corresponding to the various vibrational frequencies and simple combinations of these should show peaks on the curve. This immediately showed that the occurrence of the bands in pairs, already noted, was real, the separation being about 60 cm^{-1} . Examination of the structure of these double bands revealed that in many cases the lower frequency component of the pair was relatively sharp and often shaded to the violet, while the higher frequency component was rather stronger and broader, being itself a close doublet in

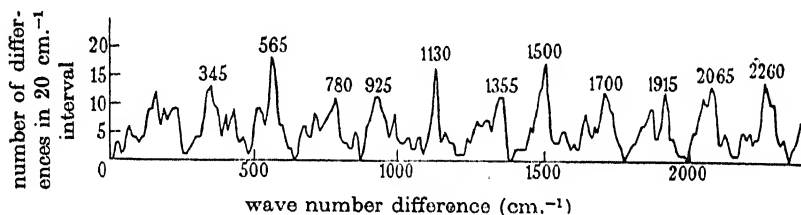


FIG. 6.

some cases. This structure is very probably due to the arrangement of the rotational branches of the band. This was accepted as a working hypothesis, and the frequency differences were re-examined, using one component only, the lower frequency component, of those bands which formed such pairs.

The grouping of the differences obtained from these selected bands was plotted as shown in Fig. 6, and shows considerable regularity. As may be seen from this figure, there are strong peaks at 565, 1130 and 1500 cm^{-1} , quite definite peaks at 345, 925, 1355, 1700, 2065 and 2260, and less certain peaks at around 160, 230, 515, 780, 1865 and 1915 cm^{-1} . It is at once obvious that within the accuracy of the measurements,

$$1130 = 2 \times 565$$

$$1700 \doteq 3 \times 565$$

$$2260 = 4 \times 565$$

and that

$$\begin{aligned} 2065 - 1500 &= 565 \\ 1500 - 925 &\doteq 565 \\ 1915 - 1355 &\doteq 565 \\ 1355 - 780 &\doteq 565 \\ 780 - 230 &\doteq 565 \end{aligned}$$

and that

$$\begin{aligned} 2260 - 1915 &= 345 \\ 1700 - 1355 &= 345 \\ 1130 - 780 &\doteq 345 \\ 565 - 230 &\doteq 345 \end{aligned}$$

It may therefore be seen that all but three of the less marked differences can be expressed in terms of three fundamental differences which would, of course, correspond to three of the vibrational frequencies of the molecule emitting the spectrum. In the choice of these three fundamentals it is, however, necessary to pass from the firm basis of observation to less certain speculation.

The 565 cm^{-1} interval was a fairly obvious first choice, as this frequency and its multiples 1130, 1700 and 2260 all show such marked peaks on the curve; this interval corresponds with the interval of around 570 used by Fowler, or around 550 to 600 cm^{-1} employed by Kondratjew in his long series. The selection of the other fundamentals from the data available is practically impossible, but the author arranged about a hundred of the strongest bands into four fairly compact arrays, which are reproduced in the original paper, using the intervals 565 and 2065 cm^{-1} .

The Origin of the Band Spectrum.

Weston has shown that the spectrum is emitted by pure dry carbon monoxide burning in oxygen. It is therefore certain that the emitting molecule can only contain the elements carbon and oxygen. It is equally certain that the spectrum is much too complex for a diatomic emitter, and in any case the various band spectra of O_2 , C_2 and CO are well known and show no resemblance to the bands of the carbon monoxide flame spectrum, so that these molecules may be ruled out. Kondratjew has discussed this question and given reasons for assuming that the bands are due to carbon dioxide.

The band spectrum of ozone, O_3 , is well known in absorption, and Johnson¹³⁵ has observed some bands in the near ultra-violet in emission using a discharge tube source, but these bands are not similar to the flame bands, and ozone may be dismissed from among the list of possible emitters.

The only other stable oxide of carbon is the suboxide, C_3O_2 . The absorption spectrum of this has been studied by Thompson and Healey²²⁷, who observed absorption between 2400 and 3300 \AA ., the region between 2800 and 3300 \AA . being banded; these bands form a few strong pairs with a separation of about 100 cm^{-1} , and a number of pairs of weaker bands with separation $50\text{--}70\text{ cm}^{-1}$. Thompson and Healey used vibrational frequencies of 840, 2160, 1227, 540, 240 and 150 in attempting an analysis. The bands lie to rather shorter wave-lengths than the carbon monoxide flame bands, but in the region in which the systems overlap there is a measure of agreement, especially with Kondratjew's measurements, which extend to shorter wave-lengths than the author's. The infra-red absorption by carbon suboxide has been studied by Lord and Wright,¹⁶⁹ who find among the strongest frequencies one of 550 cm^{-1} . Thus based purely on spectroscopic evidence it would be possible to make out a good case for C_3O_2 as the emitter; the coincidence between the band measurements is not convincing, but is as good as might be expected for a comparison between the absorption and emission spectra of a polyatomic molecule, and the doublet separation of $50\text{--}70\text{ cm}^{-1}$ and the frequency difference 540 or 550, which might be identified with the observed 565 interval, are favourable to the identity of the two systems. The chemical aspect is, however, less satisfactory; the production of a lower oxide seems unlikely and there is no positive evidence for its presence; the flame has not been observed to show the absorption spectrum of C_3O_2 ; the suboxide is supposed to decompose at 200°C . to $\text{CO}_2 + \text{C}_2$, and this should show spectroscopically by emission of the Swan bands of C_2 , which are not in fact observed in the spectrum of the carbon monoxide flame. The suboxide is not therefore likely as the emitter.

The existence of a carbon peroxide CO_3 has been presumed in certain proposed chain mechanisms for the combustion of carbon monoxide (e.g. Lewis and von Elbe¹⁶⁴). There appears to be no experimental evidence for the existence of CO_3 or other

higher oxides of carbon. Experiments by the author on the slow combustion failed to detect peroxides either chemically or by their absorption spectrum. This failure to detect the presence of peroxides is not, of course, conclusive, as short-lived compounds may be present in very small quantities and so not show absorption, although they may give strong emission spectra. Nevertheless, in view of the absence of experimental evidence for the existence of CO_3 or other peroxide, these compounds can only be regarded as a possible, but very unlikely, source of the flame bands. The spectrum of the flame of carbon monoxide burning in nitrous oxide is the same as that of the normal flame, and even though a case can be made out for the existence of a complex such as CO_3 in the combustion in oxygen, there does not seem to be any reason for supposing that it is formed in the combustion in N_2O which gives the same emission bands.

We are thus led to conclude that carbon dioxide is the most probable emitter of the bands of the carbon monoxide flame spectrum, and the implications of such a conclusion will now be fully discussed.

Carbon Dioxide as the Emitter.

In assigning the flame bands to the molecule CO_2 , as has been done by Kondratjew and by Fowler and the author⁷⁵, there are certain difficulties on the spectroscopic side. The absorption spectrum of carbon dioxide has been studied by Liefson¹⁶⁷ and by Price and Simpson²⁰², who find that the gas is transparent all through the visible and quartz ultra-violet region and that the first absorption bands lie below 1700 \AA ., and strong absorption is only observed still further to the ultra-violet. Eiseman and Harris⁵⁶ have similarly shown that liquid carbon dioxide is transparent at least to 2150 \AA . Since the usual electronic selection rules are not rigorously obeyed in the liquid state (cf. absorption by liquid oxygen), this rules out the possibility of there being any low-lying electronic levels of CO_2 . In flame sources there is not sufficient energy to excite atoms or molecules to high electronic states; thus the CO flame spectrum itself does not show well-known band systems, such as the CO Third Positive or Ångström bands or any oxygen emission which would require a fairly high excitation energy; it therefore follows that if CO_2 is the emitter the electronic transition must involve the ground state.

The emission spectrum of carbon dioxide in a discharge tube only shows the well-known band-systems of carbon monoxide, or, under negative glow conditions, a banded system which is probably due to the ionised molecule CO_2^+ . The flame bands are never observed in an ordinary discharge through carbon dioxide, although the afterglow⁷⁵, which is probably really a low-pressure flame due to recombination of CO_2 molecules decomposed in the discharge, does show the same spectrum as the flame.

If the band system is emitted by CO_2 , then, as pointed out by the author⁸⁹, there appears to be only one way of reconciling these facts, that is by assuming that the molecule has a very different shape or size in the ground and excited electronic states. The effect of a big change in the internuclear distance has been discussed in the first chapter (page 16); for a diatomic molecule it can be seen readily that the emission spectrum will lie to much longer wave-lengths than the absorption spectrum; the Schumann-Runge band-system is a good diatomic example. For a triatomic molecule there is also the possibility of a change in the shape of the equilibrium configuration, and this will have the same effect of shifting the absorption to higher frequencies and the emission to lower; thus a big difference between the regions of the absorption and emission spectra may be expected to occur more frequently for triatomic or polyatomic molecules. For example, the sulphur dioxide afterglow bands (Gaydon⁸⁸), which are known from the analysis to involve the ground state, lie around 4300 Å., while the absorption lies around 3000 Å. Thus if there is a big change in the shape or size of the CO_2 molecule in the two electronic states, the big difference between the regions of absorption (< 1700 Å.) and emission (3000–5000 Å.) could be accounted for. Also the big change in the configuration will tend to discourage excitation by electron impact (see page 20) and so, as with the Schumann-Runge bands of O_2 , and the SO_2 afterglow bands, the spectrum will not appear readily in discharge tubes. On the basis of the above discussion it will be assumed that the emitter of the flame bands is CO_2 and that the bands correspond to transitions to rather high vibrational levels of the ground electronic state.

If this is so, then the spectrum might be expected to show the frequency differences characteristic of the vibrations of the CO_2 molecule in the ground state. These are well known from the

study of the infra-red absorption spectrum (see Dennison^{50 51}). The three fundamental frequencies are ν_1 (symmetrical) about 1300 cm^{-1} , ν_2 (transverse) 667 cm^{-1} , and ν_3 (asymmetrical) 2350 cm^{-1} . Kondratjew identified the interval of about 600 cm^{-1} in the flame bands with the transverse vibrational frequency of 667 ; the analysis given by the author also shows up strongly this interval, which has a value of about 565 in the region of the spectrum studied; it is, of course, to be expected that the interval will be less than 667 for transitions to high vibrational states owing to the anharmonic factor; some of Kondratjew's intervals are between bands at higher frequency than those measured by the author, and this would account for his giving the average value of the interval as high as 600 cm^{-1} .

The other observed intervals between the flame band are less easily accounted for. If the 1500 interval, which shows a strong peak in Fig. 6, were chosen as fundamental, it could, on account of its frequent occurrence, only be assigned to the lower electronic state, and in this case could not be due to CO_2 . If, however, the 2065 interval is selected as the fundamental, as in the author's arrays, then it may be possible to identify this with the asymmetrical vibration of CO_2 , 2350 cm^{-1} . The agreement cannot be considered really satisfactory, as the discrepancy seems very large to be accounted for by anharmonic factors, but it is just possible that if the molecule is in a highly excited state of transverse vibration the asymmetrical vibrational frequency may be lowered quite considerably. The symmetrical frequency of about 1300 cm^{-1} for CO_2 is not apparent from the analysis of the flame bands. Other weak frequency differences which are observed in the flame spectrum, such as 345 or 1355 cm^{-1} , might be assigned to the upper electronic state.

The attempted vibrational analysis can therefore be reconciled to some extent with the emitter being CO_2 , but it does not prove as conclusively as might have been expected that the lowest level is involved. The analysis and interpretation is, however, complicated by lack of knowledge of the vibrational selection rules for electronic transitions in triatomic molecules (see page 18). If CO_2 is the emitter and the above explanation for the flame bands being in a different region of the spectrum from the absorption, and not occurring in discharge tubes, is correct, then it follows that the newly formed molecules, after the electronic

transition to the ground state, will be in a high state of internal vibration, i.e. they will be vibrationally activated. The method of deriving the life of these vibrationally activated molecules is given in Chapter XI, and the important bearing it will have on the cause of the afterburning of carbon monoxide is dealt with separately in Chapter XII.

The Electronic Levels of Carbon Dioxide.

It is known that since carbon dioxide is diamagnetic, the ground electronic state must be of the $^1\Sigma$ type¹⁸³ and it has been pointed out by Herzberg¹²¹ that normal CO in its $^1\Sigma$ ground state and an unexcited oxygen atom, O(3P), cannot form a CO₂ molecule in a $^1\Sigma$ state, the dissociation products from which must be of the same multiplicity in order to produce a molecule in a singlet state; hence Herzberg suggested that the dissociation products of CO₂ were CO($^1\Sigma$) and O(1D). Schmid²¹¹ disagreed with this on the grounds that CO₂ is known to be a linear symmetrical molecule and must be formed from similar oxygen atoms, the decomposition products of CO₂ being probably CO($\alpha^3\Pi$) and O(3P), giving a symmetrical construction of O(3P)+C(5S)+O(3P) for CO₂, the 5S carbon atom being in an excited state corresponding to the tetravalent state, and this argument was accepted by the author⁸⁹. Dr. Penney has since pointed out that it does not necessarily follow that CO($^1\Sigma$)+O(1D) cannot give a symmetrical molecule, and that in any case it is incorrect to regard the carbon atom as being in the 5S state, as more than one electronic state of the free carbon atom contributes to the excited tetravalent state (see page 146); nevertheless, the most likely possibility for the dissociation products of normal CO₂ under the influence of thermal agitation is O(3P) and CO($\alpha^3\Pi$). The photodissociation of CO₂ shows that an energy of about 7.3 e.v. is required as compared with 5.5 e.v. if the dissociation products were normal, the difference of 1.8 e.v. agreeing quite well with the excitation energy of atomic oxygen from the 3P to the 1D state which requires 1.97 e.v. It does not follow, however, that this photodissociation at 7.3 e.v. corresponds to the dissociation energy of normal CO₂, as the photodissociation will of course take place from an excited electronic state whose dissociation energy may not coincide with that of the ground state. The value for the dissociation energy of

normal CO_2 obtained by extrapolation of the vibrational levels (see page 144) is much higher, being of the order 13 e.v., and probably indicates that the normal carbon dioxide molecule is built up from a highly excited CO molecule.

In the combustion of carbon monoxide there is no spectroscopic evidence for this electronic excitation of the carbon monoxide, which would in any case require an activation energy of at least 138 k.cal., taking place prior to the formation of the carbon dioxide. It may therefore be supposed that in the combustion process the CO_2 molecules are formed from normal $\text{CO}(^1\Sigma)$ and oxygen and that the newly formed CO_2 molecules then undergo an electronic rearrangement to reach the ground state.

Mulliken¹⁸³ has also discussed the nature of the excited states of CO_2 , and has arrived at some very interesting conclusions; the first excited levels above the ground state are likely to be 1I and 3I , but the transition to the ground state would be forbidden by the selection rules for linear symmetrical molecules. Mulliken then proceeds to identify, tentatively, the weak absorption centred around 1600 Å. with this forbidden transition, suggesting that the selection rules might be weakened if the equilibrium form of the molecule in the upper level is triangular. This fits in well with the discussion of carbon dioxide as the emitter of the flame bands.

Quantitative Measurements.

The carbon monoxide flame is the most luminous of the ordinary flames, the light yield being greater than that from the flames of hydrogen or hydrocarbons, except, of course, when carbon deposition renders the latter luminous. Kondratjew and colleagues^{146 152 153 156} have made quantitative measurements of the light yield from the carbon monoxide flame under various conditions of temperature and composition. They find that the yield may be so high that it is equivalent to one quantum emitted for every 125 normal CO_2 molecules formed in the flame. This is very much greater than could be accounted for by thermal excitation and clearly indicates that the emission is of chemiluminescent origin.

The study of the variation of light yield with pressure reveals that the yield at first increases with pressure, reaches a maximum at around 40 mm. Hg, and then falls off. The initial rise with

pressure is interpreted as being due to a surface reaction being replaced by a homogeneous gas reaction at higher pressure, while at still higher pressure the yield falls because of quenching of the excited molecules on collision.

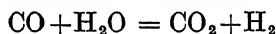
Nitrogen is found to increase the percentage combustion but to decrease the light yield, and deviations from a normal quenching curve are taken to indicate a change in the chemical mechanism, the intervention of oxides of nitrogen being likely at high pressure. The nitrogen molecules are probably excited from the ground $X^1\Sigma$ state to the $A^3\Sigma$ state by collision with the excited CO_2 molecules and then, while in the metastable $A^3\Sigma$ state, react with oxygen to form the oxides of nitrogen, as in the case of the nitrogen afterglow which shows NO bands; these oxides of nitrogen subsequently take part as catalysts in the combustion. This agrees with Bone and Newitt's conclusions based on observations of the absorption spectrum of a carbon monoxide-air explosion at high pressure which is described later (page 86).

The Effect of Moisture.

The combustion of carbon monoxide is very dependent on the presence of traces of moisture or hydrogen. The effects of careful drying are dealt with at length in Bone and Townend's book ²⁵. As the gases are progressively dried the flame speed decreases and the percentage of combustion taking place falls. For very dry mixtures ignition can only be produced by very much more energetic sparks than those required to fire moist mixtures. Ubbelohde ²³⁰ has shown that if carbon monoxide is burnt in oxygen or air at an externally heated silica jet and the gases are progressively dried, then the flame enlarges and finally goes out and cannot be relit, even though the temperature of the jet may be as high as 1400°C . Similar effects were observed with traces of hydrogen instead of water, there being a critical range between a molar concentration of hydrogen of 10^{-3} and 10^{-5} , within which the flame length varied markedly with the hydrogen concentration.

The spectrum of a normal carbon—monoxide—air flame always shows the OH bands strongly, and the most careful drying is necessary to reduce their intensity. For flames at high pressure (above 5 atmospheres) it has been shown by Weston ²⁴⁷ that the OH bands are less pronounced, and it is also known that at these high pressures the effect of drying on the combustion is

less marked. Kondratjew and colleagues^{154 155} have studied the influence of moisture on the quantity of light emitted by the flame, and find that there is a big decrease in the light yield when moisture is present. They say that this decrease cannot be explained quantitatively by assuming quenching of the electronically excited CO_2 molecules, and must therefore be due to a change in the combustion mechanism, the reaction



taking place in the presence of water. Moisture also produces a big reduction in the infra-red radiation from the flame, and this is best explained by assuming that the water molecules deactivate the vibrationally excited CO_2 molecules. The author's work on this aspect of the combustion is described in the chapter on "Afterburning."

In the reaction between dry gases at high pressure, water cannot, of course, play a part in the reaction mechanism, but there is evidence that relatively large amounts of nitric oxide are formed, this being detected both spectroscopically and chemically. Ubbelohde also speaks of the formation of ozone in the relatively dry flames. These dry flames are also influenced by the halides of the alkali metals and by platinum vapour, the flame being shorter and more diffuse under such conditions, although the percentage combustion occurring is not appreciably altered in this case, as it is with moisture or hydrogen. The continuous (CO flame type) spectrum is stated to be weakened by the presence of an alkali-metal vapour, the line spectrum of the metal appearing strongly.

The Cool Flame.

Prettre and Laffitte²⁰⁰ and Topley²²⁹ have noted that during the slow combustion of carbon monoxide, at temperatures below the ignition point, the reacting gases luminesce. This glow is described as violet or violet-red, but no observations of the spectrum appear to have been made. The presence of such a cool flame, which must, of course, be due to chemiluminescence, does, however, support the view taken by the author that an electronic rearrangement must take place in the formation of normal carbon dioxide from the monoxide and oxygen.

As already stated in the section on atomic flames, there is little reaction between carbon monoxide and atomic oxygen.

CHAPTER VII

EXPLOSION SPECTRA : THE INTERNAL COMBUSTION ENGINE

Explosions of Hydrocarbons with Oxygen or Air.

THE spectra of the explosion flames produced by mixtures of hydrocarbons, such as methane, acetylene, ethylene and propane, have been studied by several investigators (Bell ¹⁶, Smith ²¹⁹, Bone and Outridge ²⁴, Lauer ¹⁶⁰). In general, the spectra of the explosions of weak mixtures differ little from those of the inner cones of the ordinary flames, the principal features being the band systems due to C₂, CH and OH already described; the weaker bands of CH at 3143 Å. and 3628 Å. appear rather more strongly in explosion spectra, probably because of the higher temperatures attained in explosions in closed vessels. With mixtures giving more violent explosions the continuous and banded spectrum characteristic of the carbon monoxide flame is usually dominant. These violent explosions have also a tendency to excite spectra, both line spectra and bands, due to either the substance of the explosion vessel or to any dust which may be present, the sodium lines (5890 and 5896 Å.) the copper lines (3247 and 3274 Å.) and lines of iron, being frequently present, while the author has observed bands of calcium oxide in explosion tubes which had previously been rinsed with hard tap water. For over-rich mixtures carbon deposition occurs, and the spectrum then shows the usual continuum characteristic of incandescent particles.

Photographs of the flames of explosions in closed vessels show that immediately after the flame front reaches the end of the vessel there is a sudden increase in luminosity, which is strongest in the centre of the explosion vessel. This increase in luminosity, which is believed to show the carbon monoxide flame spectrum, is due to the pressure wave travelling back through the explosion vessel and raising the pressure and temperature of the gases at

the centre. The phenomenon is closely linked with afterburning and is a much-debated subject which is dealt with in a separate chapter.

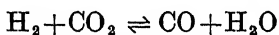
The luminous type of explosion in which the spectrum shows a continuum due to incandescent carbon particles, does not lend itself to spectroscopic study, but the conditions under which the carbon deposition occurs, as indicated by the appearance of the continuous spectrum, and the spectrum of the flame of mixtures which just do not deposit carbon, have been studied by Smith ²¹⁹ for explosions of propane and ethylene with air or oxygen. The just non-luminous flames show the Swan bands of C_2 strongly, and the mechanism of the production of these molecules in the flames seems to be related to carbon deposition, and is therefore of considerable interest because of the phenomenon of 'coking' in engines. Little that is definite can be said about the formation of C_2 molecules in flames. The subject has already been mentioned in connection with the stationary flames of hydrocarbons (page 37) and in relation to atomic flames (page 52). Smith doubts Bone and Outridge's conclusion ²⁴ that carbon deposition is primarily a function of the temperature developed in the particular mixture. A very small change in either the pressure or mixture composition results in an entire alteration of the emission spectrum from the intense "green-flame" condition in which the Swan bands predominate, to the yellow smoky flame which shows only a continuous spectrum in the visible region. Smith suggests that a thermal decomposition of the type observed for carbon suboxide, which decomposes into CO_2 and C_2 , may play some part in the formation of free carbon. The abrupt change from the green flame condition to carbon deposition may be associated with a critical change in the slow combustion processes in front of the flame, some indication of which is given by the experiments of Hsieh and Townend ¹²⁶ on cool flames and the conditions under which these change over to normal flames.

The Internal Combustion Engine ; Flame Fronts and Afterglows.

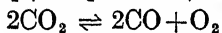
The spectra emitted by burning gasoline and other fuels in the internal combustion engine have been examined by Clark and co-workers ³³⁻³⁷ and by Withrow and Rassweiler ^{204 252}. The latter used a stroboscopic method which enabled them to

study the spectrum of the light emitted from the combustion chamber at any stage during the burning of the charge. Ordinary photographs revealed that there was a marked reillumination of the gases through which the flame had passed, this occurring during the pressure rise accompanying the rapid burning of the last part of the charge. This reillumination of the gases is referred to by Withrow and Rassweiler as the "afterglow," and is sometimes called the "afterburning" by other authors. Photographs of the spectrum show that the flame front resembles the inner cone of the ordinary stationary flame; gasoline and benzene show the usual band systems due to C_2 , CH and OH, while ethyl alcohol shows chiefly the bands of OH and CH with a trace of the stronger Swan bands, and methyl alcohol shows the OH bands and only the vaguest trace of the CH band, and no C_2 .

The afterglows of all the organic fuels studied showed only the carbon monoxide flame spectrum and the OH bands; the CH and C_2 bands are absent. This indicates that the light emitted after the flame has passed through the charge is not due to oxidation of the original hydrocarbons. The spectrum clearly indicates that the afterburning is due to the combustion of carbon monoxide, or carbon monoxide and hydrogen, and Withrow and Rassweiler suggest that the equilibria



and



are influenced by pressure and temperature changes produced by the burning of the last part of the charge. A similar afterburning phenomenon has been observed by Rassweiler and Withrow when hydrogen is used in the internal combustion engine, the radiation in this case being due chiefly to OH radicals.

Apart from theoretical applications of spectroscopy to combustion problems in engines, empirical applications are sometimes of use in determining the type of combustion which is taking place. Thus the author has found that the examination of the spectrum of the exhaust glow of an engine will sometimes distinguish between afterburning of carbon monoxide, which shows the carbon monoxide flame spectrum, and incomplete combustion of the hydrocarbons, which results in the appearance of CH and other bands characteristic of hydrocarbon combustion.

Knock.

The researches of Withrow and Rassweiler^{204 252} have also included an examination of the spectrum of an internal combustion engine under knocking conditions. As already stated, the flame front under normal non-knocking conditions shows bands due to C_2 , CH and OH, this being so for the flame in the initial stages and in the detonating zone. For knocking explosions, the spectrum sometimes shows a heavy continuum in the red, which is apparently black-body radiation, perhaps from cracking of the lubricating oil, produced by the higher temperatures reached in the knocking explosions. Withrow and Rassweiler also observed that the spectra of knocking explosions showed the bands of C_2 and CH less strongly in the detonating zone, although in the non-detonating zone the bands were emitted with almost equal intensity in the knocking and non-knocking explosions. This indicates that the difference between knocking and non-knocking explosions is confined to the nature of the burning of the last part of the charge. The possible reasons for the reduction in the strength of the C_2 and CH bands in knocking explosions, which is clearly shown by the published spectrograms, is discussed; it is concluded that the effect cannot be due to changes in the density of the gases, to physical movements of the gases, or to change of temperature affecting the thermal excitation of the radicals; the effect is therefore to be attributed to a change in the concentration of the C_2 and CH radicals resulting from a change in either the chemical reactions forming these radicals or to those consuming the radicals. Rassweiler and Withrow tentatively suggest that the removal of C_2 and CH molecules may be due to their reaction with OH radicals formed by thermal processes taking place in advance of the flame front. Since the study of the spectrum of the afterglow indicates that the hydrocarbons are burnt in the flame front it is concluded, in confirmation of results derived from flame photographs, that the whole of the sudden pressure rise which constitutes the knock is due to the rapid burning of the last part of the charge, with little or no contribution from the gases through which the flame has passed.

Thee²²⁵ showed that when lead tetraethyl is introduced into the internal combustion engine to reduce knock, the spectrum shows lines due to atomic lead ($\lambda\lambda 4057.8, 3683.5, 3639.6$) and

bands which have since been identified with lead oxide, PbO (the lead oxide bands are listed in the appendix). Withrow and Rassweiler have also observed the lead lines and oxide bands which occur in the flame fronts, and find that the lead ethyl, in addition to removing the knock, also restores the spectrum to a similar type to that of the normal non-knocking explosion, the continuum due to thermal radiation being absent and the C_2 and CH bands being restored to normal strength when knock is prevented by the addition of the lead ethyl. When iron carbonyl is introduced, lines of atomic iron, and bands of iron oxide, which are listed in the appendix, appear in the flame front spectrum.

Results obtained from the study of the absorption spectra of knocking explosions are described in a later chapter (see page 84).

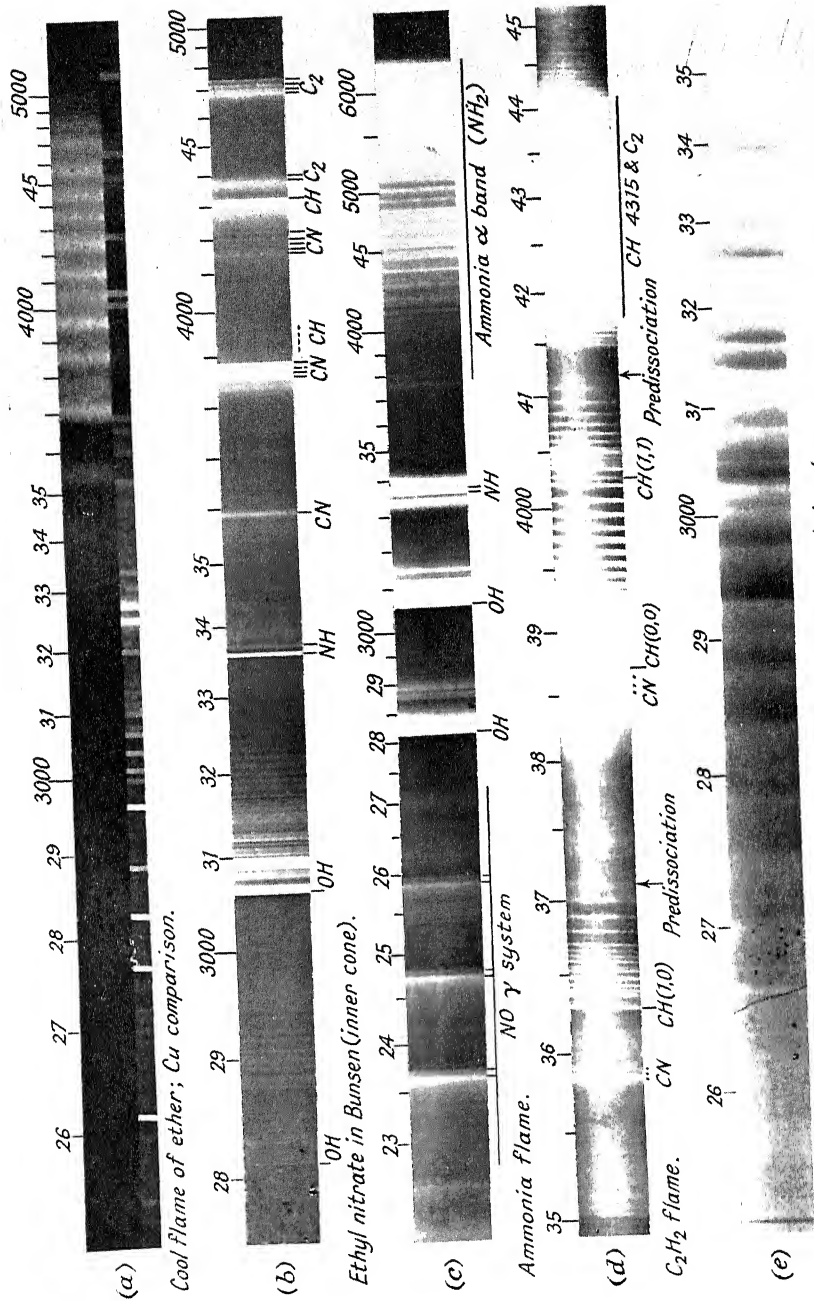
CHAPTER VIII

OTHER EMISSION SPECTRA : INORGANIC FLAMES

Nitrogen in Flames.

THE occurrence of bands due to CN, NO and NH in relatively hot flames of hydrocarbons burning in air has already been noted. The violet cyanogen bands, with sequence heads at 4216, 3883 and 3590 Å. (for description see appendix), occur very strongly in the inner cones of flames of compounds containing carbon and nitrogen, having been observed in the flames of nitrobenzene, aniline, and piperidine by Vaidya²³⁷ and in flames containing ethyl nitrate and amyl nitrite by the author (see Plate 2*b*). The bands frequently occur also in flames in which combined nitrogen and carbon are present together ; thus Barratt¹¹ found the CN bands in the coal-gas—nitrous-oxide flame, and when carbon monoxide and ammonia are burnt together in air, although the flame of carbon monoxide burning in nitrous oxide showed only the ordinary carbon monoxide flame spectrum. The cyanogen flame itself shows the violet CN bands strongly, of course, and in this case the Swan bands of C₂ have also been observed. The bands of the red system of CN, although requiring less energy for their excitation than the bands of the violet system, do not appear readily in flames, and this fact has already been commented upon (page 24). The CN radical is not, of course, the same as cyanogen, C₂N₂, and although cyanogen has occasionally been detected chemically in flames, it seems that the CN radicals are more frequently removed by reaction with other molecules than by the formation of cyanogen.

The γ bands of nitric oxide (see appendix) occur in the spectra of many flames, including those of many organic nitrogen compounds such as nitrobenzene and aniline, the oxy-ammonia flame, and the hydrogen—nitrous-oxide flame. In the last two flames the bands occur strongly in the inner cones only, but in some flames they probably extend into the outer cone.



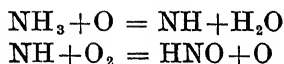
Absorption spectrum of slow combustion of pentane, showing formaldehyde bands.

Flames containing hydrogen (or moisture) and combined nitrogen usually show the NH bands at 3360 and 3370 Å. to some extent. The piled up Q branches of these bands, which form the almost line-like structures at 3360 and 3370 Å., enable the bands to be readily observed and identified. The NH bands are very strong in the oxy-ammonia flame.

The oxy-ammonia flame, a spectrogram of which is reproduced in Plate 2c, also shows a complex many-line structure in the yellow and green regions of the spectrum, which is usually known as the ammonia α band; the spectrum of the ammonia flame has been examined by Rimmer²⁰⁷, who has provisionally attributed the α band to the radical NH_2 . This band has also been observed by Fowler and Badami⁷⁴ in the hydrogen—nitrous-oxide flame.

The theory of the combustion of nitrogenous compounds has received less attention than has the combustion of hydrocarbons and other fuels, and thus, beyond establishing the existence of the radicals CN, NH and NH_2 in the combustion, the spectroscopic results have received little attention. The CN spectrum is observed strongly in flames containing combined nitrogen, but is only produced by free molecular nitrogen in very hot flames. Since the bands appear strongly when mixtures such as carbon monoxide and ammonia are burnt, as well as in the flames of organic nitrogen compounds, it may be concluded that the radicals are produced by reactions between the various radicals or atoms present in the later stages of the combustion rather than as part of the primary combustion processes, but the reactions producing the CN radicals must involve nitrogen in some form other than normal molecular nitrogen.

Semenoff²¹⁶ makes use of NH radicals in proposed reactions for the oxidation of ammonia



but a mechanism involving NH_2 (and possibly OH) would seem preferable. Many such mechanisms can be written down, but without going into the reaction kinetics and energy considerations in detail such hypothetical reactions would have little value.

The similarity of the spectrum of the carbon-monoxide—nitrous-oxide flame to that of the carbon-monoxide—oxygen flame appears to indicate a similarity in the combustion mechanism, and

shows that nitrogen compounds are not involved in the combustion in nitrous oxide. With hydrogen burning in nitrous oxide, however, the strong production of bands assigned to NH , NH_2 and NO (which are not shown by the hydrogen-air flame) appear to indicate that nitrogen compounds are actually involved in the combustion mechanism.

Cathodic Combustion.

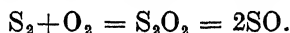
Professor Finch and colleagues have carried out a series of investigations on combustion processes in the cathode region of electric discharges through inflammable mixtures at low pressure, and have made observations⁷³ of the spectrum of the discharge with a view to finding what molecular species are present. The discharge tube spectra show the usual Ångström and Third Positive bands of CO , and they find no evidence for the presence of ionised CO , and therefore conclude that the cathodic combustion of carbon monoxide is not determined by a prior ionisation of the carbon monoxide. Under certain conditions the spectrum of the discharge showed atomic lines from the electrodes, and, when running on pure oxygen, lines of atomic oxygen and ionised oxygen atoms and molecules, and they conclude that sputtered metallic atoms and atomic oxygen may participate in the cathodic combustion; however, there was no spectroscopic evidence for atomic oxygen in discharges through the combustible mixtures, and atomic lines were only obtained with silver electrodes and not with other metals such as copper, nickel or platinum.

The Flames of Sulphur and Hydrogen Sulphide.

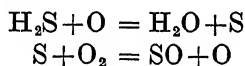
The flame spectra of sulphur and sulphuretted hydrogen have been studied by Fowler and Vaidya⁷⁶, and in both cases the strongest feature of the spectrum is the extensive band system due to diatomic sulphur, S_2 . The emission bands of SO are also feebly present in these flames, and sulphur dioxide absorption bands in the region around 3000 Å. are usually superposed on the emission spectrum of the flames. The flame of H_2S also shows the OH bands at 3064 Å., but bands of HS have not been observed in the flame, nor indeed in any source in emission, although they are known in absorption (Lewis and White¹⁶⁶).

The mechanism of the combustion is discussed briefly by Fowler and Vaidya, who say that on a peroxidation theory the

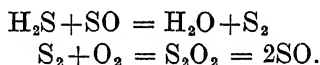
presence of the SO radicals might be accounted for by the reaction



Semenoff ²¹⁶ has proposed a chain mechanism for the combustion of hydrogen sulphide of the form,



but the absence of the line spectrum of sulphur from the flame, which is noted by Fowler and Vaidya, seems to render the above mechanism improbable. Reactions involving S_2 and SO would seem probable and the following might be possible



The Carbon Disulphide Flame.

The spectrum of the normal flame of carbon disulphide has been described in detail by Fowler and Vaidya ⁷⁶. The principal feature of the spectrum is the strong and extensive band system of sulphur, S_2 , superposed on a strong continuous background. Weaker bands due to sulphur monoxide, SO, are also observed. Absorption bands due to sulphur and sulphur dioxide are observed superposed on the emission. The flame of carbon disulphide burning in nitrous oxide shows a similar spectrum to that of the normal flame. Fowler and Vaidya have discussed the combustion processes, but many of the reaction mechanisms which they suggest appear to involve many-body collisions, and can therefore be ruled out as not being of major importance in the combustion taking place in the normal hot flame. The strength of the S_2 bands suggests that the first stage is the reaction of CS_2 with oxygen to form S_2 and an oxide of carbon. The SO bands will then be obtained from the later combustion of the sulphur, as indicated for the sulphur flame.

The spectrum of the cool flame of carbon disulphide has been photographed and measured by Emel  us ⁶¹. As with the hot flame, the strongest feature is the band system of S_2 , with the SO bands weakly but definitely present. The cool flame, however, differs from the hot flame in also showing weak bands due to the radical CS. The spectrum of the cool flame must be due to chemiluminescence, the various molecules being excited as a

direct result of the combustion processes and not by mere thermal processes. The appearance of the CS bands in the cool flame seems to indicate that the combustion process at the lower temperature is not identical with that occurring in the hot flame.

Halogens in Flames.

Vaidya ²³⁸ has observed that in the flame of methyl iodide, the green region immediately above the inner cone shows, in addition to the usual bands characteristic of organic flames, two new systems of bands (see appendix). These are apparently due to a diatomic emitter and have provisionally been assigned to the oxide IO. Similarly Vaidya ²³⁹ has found that when ethyl bromide is introduced into a flame a new system of bands, which he provisionally assigns to BrO, is obtained, together with bands due to bromine, Br₂. Flames containing methyl chloride, chloroform or carbon tetrachloride ²⁴⁰ show a band system in the ultra-violet which is identical with a system observed by Asundi and Karim ³ in discharge tubes containing carbon tetrachloride, and is known to be due to CCl. This leads the author to think that the bands attributed to IO and BrO might equally well be due to the carbon compounds CI and CBr. Urey and Bates ²³⁴ report that when chlorine is introduced into a hydrogen flame a band system is obtained which they attribute to ClO; in the absence of published experimental data on these bands it is, however, impossible to comment on their origin. Hydrogen flames containing halogens also show a strong continuous emission.

The formation of compounds such as CCl, IO and BrO in flames containing halogens may ultimately be of interest to the theory of the action of inhibitors in reducing flame speeds, as most of the best of these inhibitors contain halogens. The spectra of flames of hydrocarbons containing such compounds as propyl bromide and amyl iodide, which Dr. Zentler Gordon working in these laboratories has recently shown to be good inhibitors, are not, however, found to show any very marked differences from the normal flame spectra.

Other Inorganic Flames.

The spectrum of the flame of burning phosphorus has been studied by Emeléus and Downey ⁶⁵ and Emeléus and Purcell ⁶⁶, who find that there is a strong continuum in the visible region,

and a number of bands in the ultra-violet which, from the measurements they give, are obviously the β and γ bands of the monoxide, PO (see appendix). With the flame at reduced pressure, so that its temperature was only 125° C., the continuous portion of the spectrum was found to be less intense. Emeléus and colleagues have also examined the glow of the slow oxidation of phosphorus in air, which was one of the first recorded cases of chemiluminescence. The spectrum again shows the PO bands, but the continuous spectrum in the visible is relatively less strong. The glow of phosphorus trioxide also shows the same spectrum.

The normal flame of phosphine, and the flame at reduced pressure are stated by Emeléus⁶⁰ to show the same bands due to PO, the band at 3270 Å. (the β system) being relatively stronger than in the phosphorus flame. The hot flame at atmospheric pressure also shows the OH bands at 3064 and 2811, but these are not emitted by the flame burning at reduced pressure. There is no mention of the PH bands at around 3400 Å., and the absence of these bands tends to throw doubt on the mechanism for the combustion of phosphine proposed by Semenov²¹⁶ which involves atomic oxygen and PH radicals in the chain. It is just possible, however, that the extra strength of the β bands of PO at 3270 Å. may be due to blending with the PH bands, which were not observed separately.

The spectra of both the normal and cool flames of arsenic show, according to Emeléus^{62 64}, only a strong continuum which is strongest in the region 4300 to 4900 Å.; no bands are recorded.

The spectrum of the flame of selenium burning in oxygen shows a large number of bands superposed on a continuous background extending from the green to the violet. These bands are attributed to Se₂ and SeO₂ by Emeléus and Riley⁶⁷. They have obtained a similar spectrum from the flames of ammonia, carbon disulphide and a number of organic compounds such as ethylene, ether, acetone, benzene and alcohols burning in the vapour of selenium dioxide. These flames do not show the OH band or other emission in the ultra-violet and are quite different from the flames in oxygen.

CHAPTER IX

ABSORPTION SPECTRA

Advantages and Limitations.

THE relative advantages of using absorption spectra rather than chemical sampling as tests for the presence of unstable molecules have been pointed out by Russell ²⁰⁹ and Oldenberg ¹⁸⁹. Whereas most stable molecules have an electronic configuration resembling that of a rare gas, and consequently a high electronic excitation energy, which results in their band spectra lying in the far ultra-violet, many unstable molecules and free radicals, such as OH, NH, CN, have low-lying electronic energy levels, and show spectra in the readily accessible quartz ultra-violet region. It is, of course, just these unstable compounds which are the most difficult to make quantitative tests for chemically. By spectroscopic methods it is possible to follow quantitatively the variation with time of the concentration of certain of these unstable intermediaries. The method has, moreover, the advantage that it does not interfere with the reaction or combustion process itself, whereas chemical tests frequently necessitate stopping the reaction at various stages for sampling.

Thus, the study of absorption spectra is, potentially, a very powerful method of investigating the progress of slow combustion processes and chemical reactions in the gas phase. The method is, however, subject to certain limitations on the experimental side, the degree of the limitation varying greatly with the type of spectrum given by the molecule under study. For the purpose of the present discussion the absorption spectra may be regarded as falling into three types, (i) those with bands showing open discrete rotational structure, (ii) those with bands, the rotational structure of which is so close as to be unresolvable, at least at the head of the band, and (iii) those spectra which do not show definite band structure, but only regions of continuous absorption.

The first type, those spectra whose bands possess a resolvable

rotational fine structure, are the most difficult to handle experimentally. Such band systems may appear readily in emission and may be observed strongly and adequately on spectrographs of small or moderate resolving power, but in absorption they can only be obtained by using instruments of the highest resolving power, and even then quantitative measurements are difficult. To observe a single line of the rotational fine structure in absorption it is necessary that the focused image of the slit of the spectrograph shall be narrower than the spectrum line itself. If this is not the case the light of very slightly longer and shorter wave-lengths present in the continuous spectrum used to observe the absorption, will spread across the absorption line and prevent its observation. The natural width of a line of the rotational fine structure of a band is very small ; it depends on the temperature of the gas, on the masses of the atoms comprising the molecule, and on pressure broadening effects, these latter, however, being less important in the case of molecular spectra than for atomic lines ; the natural width is usually of the order 0.1 cm^{-1} . Thus it is necessary to use instruments of very high resolving power, such as the largest grating spectrographs, to be certain of observing bands with resolvable rotational fine structure. Molecules such as OH and other hydrides and CN and C_2 , are not readily observed in absorption in flames and similar sources because of the high resolving power necessary.

The use of spectroscopic methods for determining the presence of a molecule is more suitable when its spectrum falls into the second type, that is, the rotational fine structure of the bands is unresolvable. This is the case when the lines of the fine structure are so close that resolution becomes impossible because the spacing between the lines is less than, or at any rate of the same order as, the natural width of the lines ; this occurs most frequently at the head of the band or in the Q branch when the band is not strongly degraded in either direction. Many polyatomic molecules, in which the rotational fine structure is very close and complex, show strong bands in absorption, good examples being the band systems of benzene and formaldehyde. In these cases the absorption spectrum may easily be observed with ordinary spectrographs such as the small and medium quartz instruments in common use. The method is, in such cases, fairly sensitive and can readily be made quantitative by taking a

number of comparison spectrograms with known concentrations of the vapour. In using the method quantitatively it is usually unsafe to assume that the absorption coefficient is proportional to the concentration (Beer's law), as this is only true when the absorption coefficient does not vary rapidly with wave-length, a condition which may not necessarily be fulfilled even though the absorption may look fairly uniform with low dispersion.

For spectra of the third type, those which show regions of continuous absorption, spectroscopic determination is occasionally but rarely of use. The method is relatively insensitive, as bands of continuous absorption are not usually very strong, and thus especially refined methods of determining the intensity of the transmitted light are desirable; such methods have been used with success by Frost and Oldenberg to determine the presence of hydrogen peroxide in small quantities. Continuous spectra are less characteristic than banded spectra and therefore seldom serve to identify an unknown substance, and quantitative measurements are only of value if it is certain that the results are unaffected by absorption due to other compounds. Organic acids, peroxides, and the higher paraffins show continuous absorption at the short wave-length end of the quartz ultra-violet and ketones usually show a region of continuous absorption around 2800 Å.

For the satisfactory observation of absorption spectra a good source of continuous spectrum is required. In the visible region as far as 4000 Å., or with longer exposures as far as 3500 Å., the filament of an ordinary electric lamp is often suitable; as a brighter source a Point-o-lite lamp is frequently used; this is a very good source if the point is carefully focused on to the slit, but in some cases trouble is experienced because of the band spectra of nitrogen and ionised nitrogen which are usually emitted from the region between the poles of these lamps. For the ultra-violet region the most satisfactory source of continuum is a hydrogen discharge tube. An ordinary H type tube made of Pyrex with large aluminium electrodes is quite satisfactory if very high light intensity is not essential. As a rather more intense source the type described by Hunter and Pearse¹²⁷, which comprises a water-cooled central tube of quartz, with large aluminium electrodes sheathed in Pyrex, may be recommended. The author has found a modification of this design, giving still

more powerful illumination, satisfactory. In this modification the Pyrex electrode-sheaths were replaced by water-cooled brass ends which were lined with sheets of aluminium forming the electrodes. With a sufficiently fast flow of water this tube was able to stand up to continuous running while dissipating over 5 kilowatts. A transparent quartz window must, of course, be used on these hydrogen discharge tubes; these windows, if made of fused silica, gradually turn violet in colour and lose their transparency to the ultra-violet when the tube is used for long. If the window is strongly heated it luminesces bright green, and the violet colour disappears. It is probable that this treatment restores, at least partially, its ultra-violet transparency as well.

As an alternative to the use of a continuous source for studying an absorption spectrum, it is in some cases satisfactory to use a source giving the same spectrum in emission. In this case the intensity of the light of the particular spectrum is compared, with and without the absorption. The method has been used by Kondratjew and Ziskin^{149 150} to detect absorption by OH radicals in low-pressure flames, a discharge tube containing water vapour being used as source. The advantage of the method is that in this case absorption may be detected without the use of spectrographs of very high resolving power, as the line width of the emission spectrum will usually be comparable with that in absorption. A reliable knowledge of the natural widths of the lines in emission and absorption is, however, essential before this method can be used to obtain even approximately quantitative results.

Observations of absorption spectra relating to combustion problems have largely been confined to the region from the visible to 2300 Å. This is probably because of the falling off in sensitivity of the photographic plates in the far ultra-violet. The region between 2300 and 1900 Å. is, however, accessible on many small quartz spectrographs provided suitable photographic plates are used. The failure of ordinary photographic plates is due to absorption by the gelatine which prevents the ultra-violet light penetrating deeply, so that only the silver emulsion near the surface is affected and only very light grey records can be obtained. The difficulty can be overcome either by bathing the plate with a fluorescent material, such as medicinal paraffin or vaseline dissolved in benzene, or by using a special plate, such

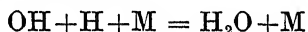
as the Ilford Q II, in which the silver emulsion is deposited on the surface. The choice of plates for this region of the ultra-violet has been discussed by Hunter and Pearse¹²⁸. The region 2300 to 1900 Å. is of particular interest because so many organic compounds which are transparent in the visible and near ultra-violet absorb in this region, and it seems very desirable that future work on absorption spectra should extend as far as possible into the ultra-violet. The absorption by oxygen sets the real ultra-violet limit, and this cannot well be eliminated. The absorption by cold oxygen at atmospheric pressure commences around 1950 Å., a number of bands degraded to the red being observed. With hot oxygen the absorption extends to longer wave-lengths, and may, if sufficient thickness of strongly heated gas is used, be obtained as far as 2500 Å., the spectrum showing much overlapping rotational fine structure, but no definite heads in this region. This absorption by hot oxygen is, however, seldom of importance in studying the absorption spectra of flames and combustion processes at wave-lengths greater than 2000 Å.

The OH Radical.

The OH band at 3064 Å. shows well-resolved rotational fine structure, and early attempts to observe this band in absorption in flames using instruments of moderate resolving power were unsuccessful. Bonhoeffer and Reichardt²⁹ obtained the band in absorption by steam at temperatures above 1200° C., and more recently the band has been observed in flames and in discharge tubes containing water vapour.

Kondratjew and colleagues^{4 149 150}, using the OH emission from a discharge tube as source, observed and measured the absorption by low-pressure flames of hydrogen burning in oxygen. From their measurements they concluded that the concentration of hydroxyl in the low-pressure flame was 1000 times that which would be produced by thermal dissociation of water at the temperature of the flame, indicating that the majority of the radicals were of chemical origin. Their calculations depend upon assumptions about the electronic transition probability, which was assumed to be of the same order as that for the sodium D lines, and the width of the lines in emission and absorption; Oldenberg and Rieke^{190 191} have commented on these assumptions, and it seems that Kondratjew's calculations may need some revision.

Oldenberg ¹⁸⁹, and Frost and Oldenberg ^{77 78} have made an important contribution to the kinetics of the reactions of OH radicals by a quantitative study of the variation of the absorption spectrum with time after the passage of an electric discharge through water vapour and through hydrogen peroxide. Light passing through the discharge tube fell on a shutter synchronised with the electric discharge so that the light from the discharge was cut off but the absorption spectrum could be examined at any desired time interval after the passage of the discharge. The second order of a 21-ft. concave grating was used to examine the spectrum, and relative estimates of the quantity of OH radicals present were made by comparing the intensities of the various lines of the rotational fine structure of the spectrum, the relative intensities of these lines being calculated from theoretical considerations. In discharges through water vapour the OH radicals were found in some cases to persist for as long as 0.4 sec., and a study of the influence of pressure, and especially of the effect of admixture of helium with the gases, led Frost and Oldenberg to conclude that the OH radicals were removed by a termolecular process, probably



although Kondratjew ¹⁴⁸ favoured the alternative reaction



followed by subsequent rapid decomposition of the hydrogen peroxide.

Oldenberg points out that the long life of the OH radicals formed by intermittent electric discharges is really due to their persistence and not to their steady formation from oxygen and hydrogen atoms; this, he says, is supported by the emission of the OH bands in the fluorescence of steam sensitised with mercury to the Hg line at 2537 Å., which could only occur as a two-stage process with the maintenance of an appreciable concentration of OH.

For discharges through hydrogen peroxide, however, the OH radicals were found by Frost and Oldenberg to persist for less than 0.01 sec., indicating their removal by a bimolecular reaction with H_2O_2 . The effect of surface reactions was also examined, and although it was concluded that clean glass walls had little effect in removing the OH radicals compared with the reaction

in the gas phase, surfaces coated with KCl were found to materially hasten the disappearance of the absorption bands.

Hydrogen Peroxide.

Hydrogen peroxide vapour shows continuous absorption in the ultra-violet, the intensity of the absorption increasing to shorter wave-lengths (Urey, Dawsey and Rice ²³⁵). The absorption is relatively weak, and the spectroscopic method would not normally be regarded as a sensitive test for its presence. Frost and Oldenberg ⁷⁷ used a cadmium photoelectric cell to measure the light intensity and examined the absorption of the mercury line at 2537 Å., using a mercury arc as source and a light filter of chlorine gas to eliminate light of other wave-lengths. With the 150-cm. long absorption tube used in their experiments they were able, as shown by calibrating experiments, to detect hydrogen peroxide at pressures as low as 0.01 mm. Observations of the absorption made in this way showed no trace of the presence of hydrogen peroxide after the passage of an electric discharge through water vapour. This clearly indicates that the considerable quantities of hydrogen peroxide frozen out in similar experiments by others workers must have been formed in the collecting trap and not in the gas phase.

The Slow Combustion of Hydrocarbons.

The absorption spectra of various hydrocarbons and related compounds undergoing slow combustion have been studied by Egerton and Pidgeon ⁵⁴. The hydrocarbons themselves are transparent throughout the quartz ultra-violet, but strong absorption was observed during their slow combustion in air. With the lower hydrocarbons, such as propane, there was an induction period of several minutes, followed by the appearance of continuous absorption (referred to as 'extinction') spreading from the short wave-length end of the spectrum. This was followed by the appearance of a banded absorption spectrum in the region 3200 to 2800 Å. which was identified with the known absorption spectrum of formaldehyde; a spectrogram taken during the slow combustion of propane is reproduced in Plate 2e. The initial extinction at the ultra-violet end, which preceded the appearance of the formaldehyde absorption, might be due to the formation of either acids or peroxidic substances which all show continuous

absorption in the far ultra-violet. Estimates of the intensity of the absorption compared with that produced by known quantities of acids found to be present by chemical titration, indicated that the main part of the extinction was due to the formation of acids, although with butane the extinction was rather stronger than could be accounted for by the known amount of acid present. This would, of course, suggest the presence, during the early stages of the combustion, of another substance, such as a peroxide, but the difference was not sufficiently marked to draw any definite conclusions.

In addition to the extinction in the ultra-violet and the formaldehyde absorption it was found by Egerton and Pidgeon, and confirmed by Ubbelohde²³², that butane and the higher paraffins showed a strong region of continuous absorption centred around 2600 Å., this absorption appearing at the end of the induction period and then dying out as the formaldehyde absorption appeared. This absorption around 2600 Å. was also observed in the slow combustion of butyl and higher alcohols and of iso-pentane, and a similar absorption was observed in the slow combustion of the ethers of tetrahydrofuryl alcohol, and α and β angelilactones. The band was not, however, observed for butyl or other aldehydes or for butylene, amylenes, or ethyl ether. The addition of catalysts such as nitrogen peroxide and amyl and ethyl nitrites was found to lower the temperature at which the absorption at 2600 Å. first made its appearance. Ubbelohde examined the absorption of a large number of compounds in attempting to identify the substance responsible for this absorption, but failed to establish its identity with certainty, although saying that its structure probably resembled that of ascorbic acid. The substance was concentrated and chemical tests showed that it did not possess peroxidic properties, although it was probably formed by the decomposition of a peroxide produced in the early stages of the combustion. Ubbelohde concluded, as a result of these spectroscopic investigations, that the formation of ring compounds containing oxygen, such as ascorbic acid, was of considerable importance in the low-temperature oxidation mechanism for the higher paraffins.

Egerton and Pidgeon note that during the slow combustion of heptane a condensation product was formed which condensed on the windows and showed absorption bands at about 2600, 2530,

2470, 2420 and 2350 Å.; it may be noted here that these bands correspond, within the accuracy of measurement, to absorption by benzene.

In the slow combustion of propane, Newitt and Baxt¹⁸⁵ have shown, by following the absorption spectrum with time, that propaldehyde is the only aldehyde present in the early stages of the oxidation. The absorption bands characteristic of the lower aldehydes (acetaldehyde and formaldehyde) being formed at a later stage in the oxidation process, the concentration of formaldehyde increasing with time. The spectroscopic method has, in this case, the great advantage that it is possible to distinguish between acetaldehyde and propaldehyde, whereas it is very difficult to distinguish between these aldehydes by chemical tests. The method also has the advantage that the progress of the reaction can be followed spectroscopically without the interruptions caused by chemical sampling, but the optical determination of aldehydes is less sensitive than some of the more refined chemical tests.

The Internal Combustion Engine.

In addition to their observations on the emission spectra of engines under knocking and non-knocking conditions (see page 68), Withrow and Rassweiler^{204 253 254} have also made a study of the absorption spectrum of an Otto cycle engine under these conditions. Using a stroboscopic method, it was shown that when the engine was knocking, the gases immediately ahead of the flame front showed strong absorption, consisting of continuous absorption in the ultra-violet upon which was superposed a banded spectrum which was later identified with formaldehyde. This absorption by formaldehyde was always observed when the engine was knocking, or was in a condition of incipient knock, but when there was no knock the absorption bands were not observed. This was found to be true of all the fuels studied. This may be taken as strong evidence that knock is due to oxidation and ignition of the gases in advance of the flame front. The gases in the flame front also showed absorption by OH radicals, but after the passage of the flame front the absorption of all types decreased rapidly.

When either isopropyl nitrite or diethyl peroxide was added to a non-knocking fuel to produce knock the formaldehyde absorption bands appeared strongly. Conversely, the addition of aniline

to prevent knocking, in a fuel which was already doing so, reduced the intensity of the formaldehyde absorption.

The action of lead tetraethyl has been studied in some detail by Withrow and Rassweiler^{254 255}. The observations were complicated by the deposition of lead compounds on the quartz window of the engine chamber and possibly by the absorption of lead tetraethyl mixed with air which was noted by Egerton and Pidgeon⁵⁴. In order to overcome the deposition of lead compounds on the window Withrow and Rassweiler used an underwater spark as source of continuum instead of the less intense tungsten lamp used in their earlier experiments; this produced a less perfect continuum, but enabled the exposure times to be reduced so that satisfactory records of the absorption could be obtained before the window became completely clouded over. It was found that when lead tetraethyl was added in sufficient quantity to prevent knock, or in even greater quantities, the formaldehyde bands were not appreciably weakened. These results are pointed out as differing from those of Egerton and Pidgeon, who found that lead ethyl prevented the formation of aldehyde in the slow combustion of hydrocarbons; this may indicate that the conditions of the slow combustion and of the rather higher temperature reactions occurring in the engine differ somewhat.

Withrow and Rassweiler found that if lead ethyl was added to a fuel which was not knocking, the presence of the ethyl did not cause the formaldehyde bands to appear, showing that the oxidation of the ethyl groups of the lead ethyl was not responsible for the maintenance of the strength of the absorption. It was suggested that in addition to inhibiting the initial stages of the combustion of hydrocarbons by which the formaldehyde is produced, the lead ethyl might also have an inhibiting action on the subsequent removal of the formaldehyde by further oxidation. Although the absorption by formaldehyde in the gases immediately in advance of the flame front was not reduced by the presence of lead ethyl, it was shown definitely that the continuous absorption in the far ultra-violet was decreased in intensity when the knock was eliminated by the addition of the ethyl, thus indicating that it had a real effect on the pre-inflammation of the gases ahead of the flame.

It has also been found that the line at 2833 Å. due to atomic

lead appeared strongly in absorption in the region immediately ahead of the flame front when lead tetraethyl was added to the fuel, but that the absorption bands of lead monoxide were not obtained in absorption under such conditions. This observation is compared with experiments on heating lead and air in a nichrome tube, the lead monoxide bands being obtained in absorption at a lower temperature than the line due to atomic lead. With lead and air heated in a carbon tube, the oxide bands were not observed, however, although the lead line appeared. These experiments are interpreted as meaning that the lead oxide formed in the engine was reduced to lead, that is, that the lead oxide acts as an oxidising agent in preventing the pre-ignition of the charge. Thus valuable information on the action of lead tetraethyl in preventing knock has been gained.

Nitrogen Compounds in Flames and Explosions.

The presence of nitrogen has a marked effect on explosions of carbon monoxide with oxygen, especially at high pressures, when considerable quantities of oxides of nitrogen are formed, and there is a big time-lag in attaining maximum pressure, accompanied by a marked exothermic effect during the subsequent cooling period. Bone and Newitt²³ have attempted to elucidate the effect of nitrogen in these high-pressure explosions by examining the absorption of the gases before, during, and after the explosion. For the observations before and after the explosion a carbon-monoxide—air flame was used as source, and the light from the explosion itself was used to determine whether there was any absorption during the progress of the explosion. With carbon-monoxide—air mixtures at 25 atm. pressure no characteristic absorption was noticed either before or during the explosion, but the banded spectrum of nitrogen peroxide (for details see appendix) showed up strongly in the absorption by the products of the explosion. This was taken to indicate that the formation of nitric oxide did not take place until after the completion of the explosion, and it was suggested that the first stage in the formation of the nitric oxide was activation of the nitrogen molecules. This conclusion agrees with that of Kondratjew (see page 63) and is probably correct, but it is unlikely that nitric oxide would have been detected in these experiments even if present, as the absorption bands of NO are only strong below 1900 Å., and even the

weak bands at 2269, 2154 and 2052 μ . are outside the spectral region studied. The observation that nitrogen decreased the intensity of the radiation from the explosion more than did other diluents is in agreement with Kondratjew's measurements on the spectrum of the flame, but the conclusion that the decrease in intensity is due to absorption is unconvincing; the ordinary carbon-monoxide—air flame does not show appreciable absorption, and the assumption that the light emitted by the combining molecules would be quantitatively independent of the nature of the diluent seems unjustified in view of Kondratjew's later work on the low-pressure flame in which it was shown that the excited CO_2 molecules are quenched by diluents such as nitrogen. It is therefore more likely that the N_2 molecules are activated by collisions with the excited CO_2 molecules rather than by absorption of radiation.

Bone and Newitt also examined the absorption by explosions of carbon monoxide with nitrous oxide and nitric oxide. In the $\text{CO} + \text{N}_2\text{O}$ explosions no absorption was observed during the explosion, but in explosions of the mixture $\text{CO} + \text{NO} + \text{N}_2\text{O}$ a new band system was observed. These bands are probably identical with a system obtained by Melvin and Wulf¹⁷⁷ in absorption by moist mixtures of nitrous and nitric oxide. The identity of the two series of bands and the nature of the emitter has been discussed by Newitt and Outridge¹⁸⁶ and Thompson²²⁷. Despite the latter's conclusions, there seems little doubt that the two systems are identical, but the emitter may be either HNO_2 or the carrier $-\text{NO}_2$.

CHAPTER X

THE INFRA-RED REGION

The Bunsen and Other Flames.

THE infra-red emission spectra of some simple flames were first examined in detail by Julius in 1890 and by Paschen around 1893. A reproduction of a typical infra-red spectrum of the ordinary non-luminous Bunsen flame is given in Fig. 7, from which it may be seen that the principal features of the flame spectrum are the strong band at about $4.4\ \mu$, and the rather wider but less intense band at around $2.8\ \mu$. Comparison with the spectra of the flames of hydrogen and carbon monoxide suggested that the main emission band was due to the combustion of the carbon monoxide fraction of the coal-gas, while the wider band at $2.8\ \mu$ was at first attributed to the burning of the hydrogen, but closer investigation revealed that this band was actually a blend of two bands, one being observed in the hydrogen flame, and the other in the flame of carefully dried carbon monoxide.

A study of the positions and identity of the principal emission bands of the Bunsen flame has been made by Barker ¹⁰, Ellis ⁵⁷, Bailey and Lih ⁷ and Hartley ¹¹⁰. The strongest band, at around $4.4\ \mu$, is found to be due to emission by carbon dioxide molecules, the absorption band of which is centred at $4.25\ \mu$. This band, which corresponds to the asymmetrical vibrational frequency of the molecule ν_3 , consists of a close doublet with maxima at 4.22 and $4.28\ \mu$ in absorption; in emission the maximum usually lies around $4.45\ \mu$, the difference in wave-length being partly due to the higher temperature of the flame, and partly due to self-absorption by carbon dioxide molecules in the cooler outer zones of the flame. Barker has calculated that, allowing for this self-absorption, the band has maxima at 4.22 and $4.38\ \mu$ in emission, giving satisfactory agreement with the width of the doublet calculated for the estimated temperature of the flame.

The broader band at around $2.8\ \mu$ is also largely due to carbon dioxide, the absorption band of which is at $2.73\ \mu$. This band is a blend of the two combination bands $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$ where ν_1 and ν_2 are the symmetrical and transverse vibrational frequencies of the CO_2 molecule respectively. The $2.8\ \mu$ emission band is also given by burning hydrogen, the wave-length of the maximum being given as $2.81\ \mu$ by Bailey and Lih for hydrogen, compared with 2.84 for the carbon monoxide flame and $2.88\ \mu$ for the Bunsen. This emission band in the hydrogen flame is usually stated to be due to water vapour, the main absorption band for which is centred around $2.6\ \mu$. The possibility of the

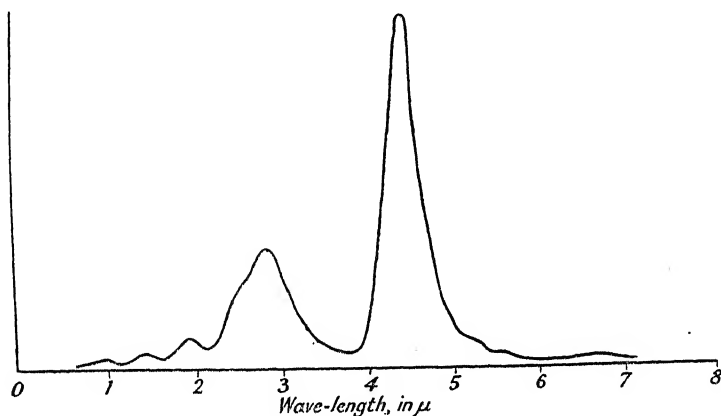


FIG. 7.

band at $2.8\ \mu$ being due in part to the hydroxyl radical does not appear to have been commented upon; the analysis of the ultra-violet emission bands of OH shows that the lowest vibrational levels of the ground electronic state are separated by $3568\ \text{cm}^{-1}$, and therefore an infra-red band in the region of $2.80\ \mu$ is to be expected; there seems no reason to doubt that the main part of the emission at $2.8\ \mu$ from the hydrogen flame is due to water vapour, but in view of the relatively long life of OH radicals, demonstrated by Oldenberg, it is possible that infra-red emission or absorption by OH may influence the position of the maximum of the band obtained in the flame.

In addition to the two main emission bands, the Bunsen flame shows a number of much weaker maxima and inflections. Bailey

and Lih have compared the emission spectra of flames of hydrogen, carbon monoxide and methane with the Bunsen flame, and attribute weak bands at 0.95, 1.45, 5.3, 5.5 and 6.7 to the burning of hydrogen, while a band at 1.99 μ occurs only in flames containing carbon compounds and has been identified by Ellis with the weak absorption band of carbon dioxide at 2.02 μ .

Although the strong absorption bands at 4.25 and 2.7 and the weak band at 2.02 of carbon dioxide appear readily in the emission spectrum of the flame, the other strong absorption band of carbon dioxide at 14.9 μ has not, apart from an observation of a band at 14.1 μ by Rubens and Aschkinass in 1898, been observed in emission; Bailey and Lih examined this region of the spectrum and suggested that their failure to observe the band might be due to either a thin film of collodion on their prism, or to atmospheric absorption; Garner and Johnson⁸² examined the spectrum of the carbon monoxide flame in this region and failed to observe the band, although they say that the sensitivity of their instrument was such that an intensity one fiftieth of that of the band at 4.4 μ would have been sufficient for detection. The failure to observe this band can be explained in terms of the long life of molecules in the state of vibration corresponding to the emission of this band, and this is of great interest in view of the author's theory of the afterburning of carbon monoxide and is referred to again in the appropriate chapter.

The shift in the wave-length of the main bands at 4.45 and 2.8 μ from the values of 4.25 and between 2.6 and 2.73 in absorption, and the variation of the wave-length in different flames has received a good deal of comment, and has been largely attributed to the effect of temperature. The higher temperature in the emission sources will, of course, result in more excitation of the higher rotational levels so that the width of the separation between the peaks of the P and R branches, usually known as a Burmeister doublet, will be greater in emission, but the shifting of the band to longer wave-lengths produced by the higher rotational temperature should not be important. The absorption band of CO₂ at 4.25 μ corresponds to a change of the asymmetrical vibrational quantum number v_3 from 0 to 1. In emission the band at 4.25 corresponding to v_3 changing from 1 to 0 will have superposed on it a number of bands due to transitions between higher values of the vibrational quantum numbers. Calculations

based on formulae given by Adel and Dennison ¹ show that bands corresponding to changes of v_3 from 2 to 1, from 3 to 2 and from 4 to 3 should be centred about 4.30, 4.34 and 4.38 μ respectively; the other vibrational frequencies of CO_2 may also be excited, and, provided the quantum numbers for these do not change, other bands due to unit change of v_3 will be present in the flame spectrum and these will all lie to longer wave-lengths than 4.25 μ . The fact that the centre of the band lies around 4.45 for most flames suggests that the asymmetric vibration of CO_2 is highly excited under flame conditions. The position of the maximum is also, however, very much modified by self-absorption by the cooler gases surrounding the flame. The effect of this self-absorption is very marked in the curves for explosion flames published by Garner and Johnson ⁸², and calculations on the effect of the self-absorption in influencing the position of the maximum of the band at 4.4 μ have been made by Barker.

The infra-red emission spectra of flames of gases burning in nitrous oxide have been studied by Bailey and Lih ⁸. With carbon monoxide or coal-gas the emission spectrum did not differ significantly from that of the corresponding flames in air, a strong band being observed at 4.50 μ and a less intense band at 2.88 μ . With hydrogen, premixed with nitrous oxide, burning in air the normal hydrogen-air spectrum was obtained, but with hydrogen burning in the nitrous oxide the spectrum was quite different, there being a strong band at 4.75 and bands of moderate intensity at 4.00 and 5.49 μ in addition to the water vapour band at 2.7 μ and other weak bands due to this molecule. The bands at 4.75 and 4.0 are probably due to nitrous oxide, which shows absorption bands not far from these wave-lengths. The band at 5.49 was tentatively identified with water vapour by Bailey and Lih, but the agreement is unconvincing, and it seems not unlikely that this band may be due to nitric oxide, which shows absorption at 5.3 μ .

The identity of the various infra-red emission bands with the absorption bands of the products of combustion, and Paschen's observation that heated carbon dioxide emitted approximately the same bands as the carbon monoxide flame, appear at first sight to point to a thermal origin for the radiation. However, it must be remembered that the radiation from carbon dioxide molecules will always be characteristic of the vibrational fre-

quencies of this molecule, irrespective of the cause of the excitation. It seems, indeed, that in general the radiation is due partly to thermoluminescence, and partly to chemiluminescence, although the distinction between the two forms is rather arbitrary. It is obvious that the freshly formed molecules will tend to be at a higher effective temperature than the surrounding molecules until they have had time to reach thermal equilibrium with their surroundings, and any lack in equipartition of the energy among the various possible forms which it may take may be regarded as energy of activation of the molecule, and emission of this energy may then be termed chemiluminescence, although it differs in no way from ordinary thermal radiation. Thus, if, as is suggested in the chapter on the afterburning of carbon monoxide, the newly formed CO_2 molecules are vibrationally activated as the result of the combustion process, then the radiation may be equally well termed chemiluminescence or thermoluminescence corresponding to a rather high effective vibrational temperature of the newly formed molecules.

Relative Intensities of Bands.

The relative intensities of the two most important bands at 4.4 and 2.8μ vary somewhat in various sources. In the Bunsen flame it has been shown by Hartley¹¹⁰ that the 2.8μ band is stronger, relative to the 4.4μ band, in the inner cone than in the outer. In this case the band at 2.8μ is no doubt partly due to water vapour, and the greater relative strength of this band in the inner cone is in agreement with the chemical evidence which indicates that the outer cone is chiefly due to carbon monoxide burning to the dioxide. The ratio of intensities of the two bands depends on the temperature and condition of the flame as well as on the fuel. Bailey and Lih⁷ record that the ratio of the intensities of the 4.4μ band to the 2.8μ band is 2.8 for coal-gas in a Bunsen flame, but 3.5 for a Meker burner; the carbon monoxide flame gives a value around 8.1, varying somewhat with the dryness of the gas, while for methane the 4.4μ band is rather surprisingly given as high as 10.0 times as intense as the 2.8μ band. For flames of mixtures of carbon monoxide and hydrogen the relative strength of the 4.4μ band at first rises with concentration of carbon monoxide, being 9.6 times as strong as the other band for flames containing 90% of CO, but decreasing again to 8.1

for flames of pure carbon monoxide. The effect of moisture in altering the relative intensities of the bands in explosion flames of carbon monoxide has also been noted by Garner and Johnson⁸². These results are no doubt affected to some extent by self-absorption by carbon dioxide and water vapour surrounding the flames, and the temperature would naturally be expected to have some effect in determining the relative intensities of the bands, the band at $2.8\ \mu$ being favoured by higher temperature. Schaefer and Phillips recorded the ratio of the intensities of the bands as 28.5 for absorption by carbon dioxide. Comparison of relative intensity values given by different authors is rather meaningless owing to the effect of instrumental resolving power on the apparent strength of the bands, but it seems curious that the band requiring higher energy for its excitation, the $2.8\ \mu$ band, should appear not less than a tenth as strong as the $4.4\ \mu$ band in emission, while in absorption it is only a twenty-eighth as strong. It seems clear that the relative strength of the bands is determined by the chemical reaction rather than purely by thermal excitation.

The Quantity of Energy Radiated by Flames.

By far the greater part of the energy radiated by flames lies in the infra-red, the visible and ultra-violet emission accounting for only a small fraction of the total energy emitted, the radiant efficiency in the visible being only about 0.4%. The actual quantity of energy radiated varies rather considerably with burner design and the degree of aeration of the flame, and this necessitates care in the comparison of results. Measurements of the total amount of energy radiated have been made by Helmholtz, Callendar, David and others, and many of the more important features of their results have been conveniently summarised by Hartley¹¹⁰. The carbon monoxide flame yields the greatest amount of radiant energy, although the measurement, as will be seen later, depends very much on the degree of dryness of the gas. Helmholtz showed that moist carbon monoxide radiated about 2.4 times as much as the hydrogen flame for a given volume of gas burnt, and that the amount of radiation from such flames as methane, ethane, and coal-gas could be calculated approximately from the number of carbon dioxide and water-vapour molecules formed, using the results for the flames of carbon monoxide and hydrogen.

Hartley gives curves for the amount of energy radiated by coal-gas flames for varying degrees of aeration of the flame, and reproduces similar curves previously determined by Callendar. For very high aeration of the flame the amount of energy radiated is about 10% of the total energy set free by the combustion, and rises to a value of about 18% for normal full aeration, and then falls slightly, to rise again when the aeration is decreased so that the flame becomes luminous. Hartley's measurements indicate that about a seventh of the radiation comes from the interconal gases, and about six-sevenths from the outer sheath.

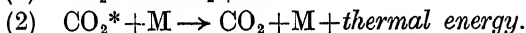
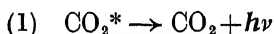
The percentage of the energy of combustion which is radiated has been shown by David to depend on the pressure of the gas, the amount of radiation falling with increase of pressure. An interesting observation first made by Helmholtz and confirmed by Haslam, Lovell and Hunneman¹¹¹ is that preheating of the gases reduces the amount of energy radiated by the flame. The preheating must of course raise the temperature of the flame, and the lowering of the amount of radiation suggests that the emission of the radiation is not therefore purely due to thermal causes.

The radiation from the carbon monoxide flame depends on the presence of hydrogen or moisture. The presence of water vapour has, however, little effect on the radiation from the hydrogen flame, the total radiation from explosion flames of which is given by Garner and Tawada⁸⁷, for a theoretical mixture at atmospheric pressure, as 2% of the total available energy. It is found that nitrogen, oxygen and argon, when present as diluents, slightly increase the amount of energy radiated, while the addition of helium or extra hydrogen reduces the radiation. These results can be explained in terms of the thermal conductivities of the gases, and indicate that for the combustion of hydrogen the radiation is largely due to thermal causes, differing in this respect from the carbon monoxide flame.

Carbon Monoxide Explosion Flames ; Effect of Catalysts.

The quantity and quality of the infra-red radiation from explosion flames of carbon monoxide-oxygen mixtures, and the effect of catalysts on this radiation, have formed the subject of a long series of experiments by Garner and colleagues^{14 80 82 84 85 86}. The infra-red emission spectrum of these explosion flames is similar in general character to that of the stationary flame, but

for the explosion flame the 2.8μ band is relatively more intense, being usually rather stronger than the 4.4μ band. When the gases are carefully dried there is a very marked increase in the total radiation emitted by the explosion, and the 4.4μ band becomes relatively stronger. In one of their earlier papers Garner and Johnson show that the radiation for wave-lengths other than those around 4.4μ is increased about 60% by drying, while the intensity of the radiation at the maximum of the 4.4μ band is greater by a factor of 4. The total infra-red radiation was about 2.5 times as great for the dry flame as for the moist one, and in later experiments with improved drying the effect appeared to be even more marked. It was shown that the absorption by water vapour in the region of 4.4μ is negligible, and could not therefore account for the effect. It is difficult to completely rule out possible alterations of the absorption by the other gases present, but the known high transparency of the ordinary Bunsen flame to its own radiation and the observation that the absorption spectrum of the unburnt gases in the region of the spectrum of interest was not affected by the presence of water, led Garner and Johnson to suggest that the effect was due to the water-vapour molecules deactivating the vibrationally excited CO_2 molecules, and thus preventing them from radiating. If CO_2^* represents a vibrationally activated CO_2 molecule, then either of the following processes may occur



where $h\nu$ represents radiant energy and M is a third body. With M as either oxygen, nitrogen or carbon dioxide, it seems that the second process is relatively slow, allowing a considerable amount of radiation to occur by the first process, but if the third colliding body M is a water molecule, then the second process is much more rapid and the vibrational energy of the carbon dioxide molecules is rapidly converted into thermal energy and the radiation from the explosion flame is correspondingly reduced. This agrees with the observation that the temperature of carbon monoxide flames is raised appreciably by the presence of traces of moisture or hydrogen.

In addition to the marked effect shown by water and hydrogen in reducing the infra-red radiation, many other catalysts are also

active in this respect, the effect produced by ethyl nitrate or ethyl iodide being even greater than that for water, and Garner, Johnson and Saunders report that in this case the total infra-red radiation may be reduced to as little as 1% of that emitted by the dry explosion flame. Chloroform and nitrogen peroxide also behave as weak positive catalysts, but carbon tetrachloride acts as a negative catalyst, the infra-red radiation being increased when a little CCl_4 is added to a mixture of dry carbon monoxide and oxygen, while the flame speed and maximum temperature attained by the mixture are correspondingly reduced.

The correspondence between the reduction in the infra-red radiation and the increase in flame speed produced by various catalysts is well shown by the measurements of these quantities collected together for comparison in Table 3. This shows the radiant energy for the explosion flame of a mixture of pure dry carbon monoxide and oxygen and for similar flames with small amounts of catalyst added, together with the corresponding flame speeds. The loss in radiant energy from the flame front results in there being less energy available for the initiation of the combustion processes, and hence the strong radiation from the pure dry mixtures results in a reduction in the velocity of propagation.

TABLE 3

Catalyst	% catalyst	Radiation cal. $\times 10^4$	Flame speed cm./sec.
—	0.00	6.00	100
H_2O	0.23	2.76	780
H_2O	0.44	2.39	900
H_2O	1.95	1.63	> 1000
$\text{C}_2\text{H}_5\text{NO}_3$	0.28	2.30	930
$\text{C}_2\text{H}_5\text{NO}_3$	0.46	2.20	> 930
$\text{C}_2\text{H}_5\text{NO}_3$	0.89	1.56	2500?
$\text{C}_2\text{H}_5\text{I}$	0.18	2.16	> 800
$\text{C}_2\text{H}_5\text{I}$	0.32	1.67	1100
CHCl_3	0.47	2.30	560
CCl_4	0.35	6.34	79
CCl_4	0.72	6.60	44
CCl_4	1.42	6.47	55

The effect of hydrogen on carbon-monoxide—oxygen explosions has been the subject of exhaustive study by Garner and colleagues. There is a reduction in the total radiation from the explosions of the carefully dried mixtures when hydrogen is present, this

being partly a gradual fall in the emission with increasing concentration of hydrogen and partly an abrupt fall which occurs at a critical percentage of hydrogen. For low concentrations of hydrogen, below this abrupt fall, the decrease in the infra-red emission produced by the hydrogen is attributed to deactivation of the vibrationally activated molecules of carbon dioxide produced in the combustion process; this explanation is similar to that given above for the effect of water on the emission.

The abrupt fall in the radiation which occurs at a critical concentration of hydrogen varies with the initial pressure of the explosive mixture. At atmospheric pressure the fall, or "step" in the radiation-pressure curve, as it is called by Garner, occurs at a concentration of 0.03% of hydrogen, and moves to greater hydrogen concentrations as the pressure of the explosive mixture is reduced. The probable cause of this step has been the subject of much discussion in the later papers, and it is concluded that for concentrations below the step the explosion flame is propagated by the combustion of carbon monoxide directly with oxygen, while at higher concentrations of hydrogen the flame is propagated by a mechanism in which the hydrogen takes part, the step occurring at the hydrogen concentration for which the flame speeds due to the two processes are equal. Garner and Pollard suggest a chain mechanism involving atomic hydrogen, produced by collision of activated CO_2 molecules with hydrogen molecules, for the reaction at relatively high concentrations of hydrogen, and explain the effect of a number of diluents, such as carbon dioxide, chlorine, bromine and carbon tetrachloride in terms of the chain-breaking and drying of the products by removal of water molecules. Measurements of the variation of ionisation of the gases with time, as the flame front passes by, indicate a double maximum of ionisation for pressures of hydrogen below the critical "step" concentration, this supporting the view that the step corresponds to the equality of flame speeds of two different mechanisms.

The variation with pressure of the radiant emission of dry mixtures of carbon monoxide and oxygen has been examined. The pressure-radiation curve is shown by Garner and Hall to be approximately linear, but intercepts the pressure axis at about $p = 12$ cm. instead of passing through the origin. This is interpreted as meaning that the infra-red radiation from the carbon

monoxide flame is, at least in part, due to chemiluminescence and not only to thermal emission. It is stated that the intercept can be explained if the activated molecules have a life of the order 10^{-3} sec., or rather less if the energy can be rapidly transferred from one CO_2 molecule to another. These conclusions are supported by the influence of various inactive diluents. Helium has a very high thermal conductivity and decreases the infra-red radiation, indicating that some of this is of a thermal nature, but oxygen, nitrogen, carbon monoxide and argon all increase the amount of energy radiated to some extent, and this can only be explained by assuming that a large part of the energy emitted is luminescence from the newly formed molecules of carbon dioxide.

The Rate of Emission of Radiation from Explosions and Engines.

The rate of emission of infra-red radiation from various explosive mixtures has been measured by David ⁴¹, who used filters of glass, quartz and fluorite to separate the radiation in the two principal bands at 4.4 and 2.8 μ . It was found that for coal-gas—air explosions the radiation of wave-length 2.8 μ decreased more rapidly after the explosion than the radiation at 4.4 μ . David concluded that the large amount of radiation from coal-gas—air and hydrogen—air explosions was mainly of thermal origin. The dependence of the ratio of the intensity of the 2.8 and 4.4 μ bands on the mixture strength rather than on the temperature attained in the explosion led David to conclude that there was a lag in the equipartition of the internal energy of the newly formed molecules among the various vibrational and rotational degrees of freedom.

Measurements of the rate of radiation for explosions of carbon monoxide have been made by Garner and Johnson ⁸³, who found that, within the limit of accuracy of their measurements, the strong emission of radiation coincided with the duration of the flame and fell abruptly to a small residual value when the flame became extinguished. They concluded, therefore, that for dry, slow-burning, mixtures the radiant energy has its origin in the flame front where the chemical change is proceeding, and not in the hot products of the reaction. For the moist, faster burning, mixtures the radiation outlasted the period of inflammation;

in this case the flame temperature was higher, so that a considerable proportion of the radiant energy may be of thermal origin.

Thus all these observations on the infra-red radiation seem to show clearly that while for the explosion of mixtures containing hydrogen, the radiation is mainly thermal, that from the combustion of dry carbon monoxide is of chemical origin.

In addition to the experiments on the radiation from explosions of various gas mixtures reviewed above, measurements of the rate of emission of infra-red radiation from the internal combustion engine have been made by Steele ²²². Using a stroboscopic method and various filters to cut out certain regions of the infra-red spectrum so that the amount of radiation in the bands at 4.4 and 2.8 μ could be compared, Steele measured the radiation at various crank angles of the engine. He found that the radiation continued to rise for some 20° of crank angle after the attainment of maximum pressure, and this was taken as evidence of the formation of metastable molecules of H₂O and CO₂.

CHAPTER XI

THE LIFETIMES OF ACTIVATED MOLECULES

THE importance of a knowledge of the radiative and collision lifetimes of activated molecules has been stressed in Chapter II. These factors control not only the intensity of the various band spectra emitted by flames, etc., but also the combustion process itself, determining which of the many possible chemical reactions which can take place in the flame is actually dominant. Energy chains in particular depend on the energy-rich molecule retaining its energy, so that it is not lost either by radiation or collision with other types of molecule, until it is used in the particular type of collision which propagates the chain. The formation of collision complexes, and the stability of polyatomic molecules with a large amount of internal energy are also of importance in determining the kinetics of the combustion processes. In this chapter indications are given of the methods by which the radiative and collision lives of activated molecules may be determined, and such scanty data on actual molecules as are available are mentioned and discussed.

The Derivation of the Radiative Lifetime.

An excited atom or molecule will, if it is left undisturbed, eventually emit its excitation energy as electromagnetic radiation. The average life of the excited atom or molecule before this act of radiation occurs can be calculated from a quantitative knowledge of the absorption spectrum. The deduction of the appropriate formula is based on Einstein's derivation of the Planck Radiation Law, and is, for our purpose, most conveniently expressed in the form given by Tolman ²²⁸.

The probability A_{21} that an atom or molecule in energy state 1 will undergo a transition to state 2 with emission of radiation of frequency ν is given by the expression

$$A_{21} = \frac{8\pi\nu^2}{c^2 N_1} \cdot \frac{p_1}{p_2} \int_0^\infty \alpha \cdot d\nu$$

where N_1 is the number of molecules per unit volume in state 1 (the initial state for absorption), c is the velocity of light in cm./sec., ν is the frequency of the radiation expressed in cm^{-1} (i.e. the wave-number of the absorption band), p_1 and p_2 are the *a priori* probabilities of the two states, and α is the absorption coefficient.

If only the one transition from state 2 is possible, i.e. the transition to state 1, then the average life of the excited atom or molecule τ is simply the reciprocal of the transition probability

$$\tau = 1/A_{21}$$

while if transitions are possible from state 2 to a number of other states, a , b , c , etc., the reciprocal of the mean life will be equal to the sum of the transition probabilities

$$1/\tau = A_{2a} + A_{2b} + A_{2c} + \text{etc.}$$

In order to determine the probability A_{21} from the formula given above, a knowledge of the number N_1 of atoms or molecules in the initial state for the absorption, the *a priori* probabilities of the states, and $\int \alpha \cdot d\nu$ is necessary.

The number of molecules in any particular state with energy E will be proportional to the usual Boltzmann factor

$$e^{-E/kT}$$

where k is Boltzmann's constant, and T is the absolute temperature. Thus if all the low-lying energy levels of the molecule with their *a priori* probabilities are known, it is possible, by assuming a value for the absolute temperature, to calculate the proportion of the total number of molecules in the required state 1. From this and from a knowledge of the pressure and temperature of the absorbing gas and the number of molecules per cubic centimetre at N.T.P. (Loschmidt's number) it is possible to determine the actual value of N_1 .

An energy level which can be specified by a single set of quantum numbers has an *a priori* probability of one, but if there is any degeneracy, so that the energy level in reality consists of two, three, or more superposed levels, then the *a priori* probability takes the values 2, 3, or more, as the case may be. For the determination of this *a priori* probability, or statistical weight as it is often termed, reference must be made to the more advanced

textbooks on molecular spectra. For a series of rotational energy levels of a diatomic molecule it follows from the quantum theory that any level with rotational quantum number J will be split into $2J+1$ sublevels which will coincide in the absence of an external field, so that each level has a statistical weight of $2J+1$ times that for a state with $J = 0$.

If light of intensity I_0 is incident on a layer of absorbing gas of thickness l , then the intensity I of the transmitted light will be

$$I = I_0 e^{-\alpha l}$$

this expression defining the absorption coefficient α . If the values of the absorption coefficient α are measured for all frequencies ν in a particular absorption line or band, then the total absorption

$$\int_0^{\infty} \alpha \cdot d\nu$$

may be obtained by plotting α against ν and integrating graphically. Where this is not possible an approximation can be made if the absorption coefficient at the centre of the absorption line α_m is known and also the half width of the line

$$\int \alpha \cdot d\nu = K \cdot \alpha_m \cdot \Delta\nu$$

where $\Delta\nu$ is the width of the line, and K is a constant whose exact value depends on the contour of the absorption line but which usually has a value not far from $\pi/2$.

This method of determining the transition probability, and thence the radiative life, may be applied to either a single absorption line of the rotational structure, or to a whole band, the difference in the values for the total absorption $\int \alpha \cdot d\nu$ being counterbalanced by the difference in the number N_1 of molecules in the initial level from which absorption takes place. The evaluation of N_1 , while not difficult for a diatomic molecule, requires more care if a single line of the rotational structure is being used for the determination than when the whole band is used. When a whole absorption band is used it is often sufficient to assume that at room temperature all the molecules are in the lowest vibrational level so that N_1 becomes identical with the total number of molecules per cubic centimetre in the gas. The value of the transition probability and mean radiative life must

in this case be regarded as a sort of rough average for all the possible transitions from the various rotational levels of the molecule in the excited state, but this is often sufficient, and indeed nearer the requirements of the combustion theory, which is seldom, if ever, interested in the radiative life for a particular rotational level.

The weakness of this method of determining the radiative life of a molecule is the experimental difficulty in measuring the absorption coefficient with sufficient accuracy. The natural width of a line of the rotational fine structure of the spectrum of a molecule at atmospheric temperature is very small, and for a satisfactory measurement of the absorption in the centre of the line the very highest resolving power available is barely sufficient. The need for the use of high resolving power in making observations of absorption spectra has already been stressed. The absorption coefficient at the centre of a line is very high, and any overlapping of the light of neighbouring wave-lengths may reduce this absorption coefficient by a factor of several powers of 10 and reduce the value of $\int \alpha \cdot d\nu$ so that the calculated value of the radiative life is much too high.

In some cases, instead of calculating the transition probability A_{21} as given by Tolman's formula, authors who have made quantitative measurements on absorption spectra have determined the "f value" for the absorption lines. On classical electron theory the total absorption $\int \alpha \cdot d\nu$ is related to the total number of disperse electrons N_{el} per cubic centimetre by the expression

$$N_{el} = \frac{mc^2}{\pi e^2} \int_0^\infty \alpha \cdot d\nu$$

and for a number N_{rad} of molecules absorbing the radiation the ratio $N_{el}/N_{rad} = f$, the oscillator strength. This "f value" is related to the transition probability A_{21} by the expression

$$A_{21} = \frac{p_1}{p_2} \cdot \frac{8\pi^2 e^2 \nu^2}{m \cdot c} \times f$$

where e is the electronic charge, m the electronic mass, and ν is again expressed in cm^{-1} , so that

$$A_{21} = \frac{p_1}{p_2} \cdot \nu^2 \times 0.67f.$$

Values of Radiative Lives.

The most interesting calculation of the radiative life of an electronically excited molecule is, from the combustion viewpoint, undoubtedly the determination of the life of excited OH radicals made by Oldenberg and Rieke^{190 191}. They used the second order of a 21-ft. concave grating spectrograph to study the absorption by a mixture of steam and oxygen heated to 1200° c. The concentration of OH radicals was calculated from available data on the dissociation of water, and the absorption was measured quantitatively for various lines of the 3064 Å. band of OH. The resolving power of the spectrograph used was 0.145 cm^{-1} , compared with an observed line width of 0.58 cm^{-1} , and by comparing the observed intensities of various lines, whose intensity ratio was known theoretically, and making a small correction, Oldenberg and Rieke were able to obtain f values for the various lines which they believe to be accurate to within about 15%. From these f values they calculated the mean lifetime for the rotational level $J = 4\frac{1}{2}$ of the lowest vibrational state of electronically excited OH as 3.8×10^{-6} sec. The several possible transitions from this rotational level to the rotational levels of the ground state in its lowest state of vibration were taken into account, and it was assumed that since for OH the (0, 0) band is very strong compared with the (0, 1) band it was safe to neglect other possible transitions to higher vibrational levels.

This value of around 4×10^{-6} seconds is also in agreement with fresh calculations by Oldenberg and Rieke on Avramenko and Kondratjew's observations of the absorption spectrum of OH, using the emission line reversal method. This value for the lifetime is about a thousand times as long as that computed from the radiation damping of the corresponding electromagnetic dipole, from which Oldenberg and Rieke conclude that the transition for OH is half forbidden. They say that the dissociation products of normal and excited OH are probably $\text{O}(^3P) + \text{H}(^2S)$ and $\text{O}(^1D) + \text{H}(^2S)$, and the transition is partly forbidden because the atomic transition 3P to 1D is not allowed.

White²⁴⁸⁻²⁵⁰ has made quantitative measurements on the violet bands of CN as obtained in absorption from cyanogen in discharge tubes. In this case the f value is considerably higher than for OH, and White says that the average value of f is about

0.1 with an experimentally observed lower limit of 0.026. Taking the value of f as 0.1, the author has obtained a value for the radiative life of the excited CN radicals by making the following assumptions :

$$\nu = 25,800 \text{ cm}^{-1};$$

$p_1/p_2 = 1$; the actual value is $(2J+1)/(2J+3)$ for the R branch and $(2J+1)/(2J-1)$ for the P branch, and as the rotational quantum number J becomes large, both these expressions approach 1;

transitions from the upper $^2\Sigma$ level of the violet bands to the $^2\Pi$ upper level of the red system may be neglected;

two transitions, corresponding to the lines of the P and R branches, are possible from each rotational level;

the (0, 0) band at 3883 Å. is at least twice as strong as all other transitions from the $v' = 0$ level.

These assumptions lead to a value for the radiative life of excited CN of rather less than 1×10^{-8} sec. This relatively short mean life is probably the reason for the ease with which the violet CN bands occur in flames and other sources.

Comparatively few other calculations of radiative lives or f values are available for electronic transitions in molecules. The f values for the Li_2 molecule have been determined by Ladenburg and Levy¹⁵⁹, who found values of between 0.008 and 0.045 for individual lines. Although the f values are rather small, the large number of possible vibrational transitions from each level which may occur for this spectrum must reduce the radiative life, which is again probably of the order 10^{-8} sec. For the I_2 molecule, f values of the order 10^{-6} were obtained by Füchtbauer and Hofmann, but Oldenberg and Rieke point out that a correction for the number of molecules in the initial levels would increase this value to around 10^{-4} . The radiative life is probably of the order 10^{-6} sec. For atomic lines corresponding to fully allowed transitions the f values approach 1, and the radiative lives are then of the order 10^{-8} sec., while for half-forbidden intercombination lines like the mercury line at 2537 Å. the radiative life is longer. It seems that generally for electronic transitions in molecules the radiative life will be of the order 10^{-8} sec. if the transition is fully allowed by both the selection rules for the electronic states of the molecule and for the tran-

sition between the atomic states corresponding to the dissociated molecule.* If the transition is allowed on the usual selection rules for molecules, but the electronic transition is not allowed for the atoms when the molecule is dissociated, then the radiative life may be increased †, perhaps, to something of the order 10^{-6} sec. If the transition is partly forbidden by the molecular selection rules, then the radiative life will be very much longer still; this is probably so for the $a^3\Pi$ level of carbon monoxide, the only possible transition from which is to the 1Σ level, corresponding to the emission of the Cameron bands, which are always weak on account of the change in the multiplicity. For genuine metastable states the radiative life may be assumed to be infinite compared with the collision life under normal conditions.

For atomic lines corresponding to allowed transitions the f values, and therefore the radiative lives, are affected by the presence of foreign gases, the electromagnetic fields of neighbouring molecules perturbing the energy levels so that the transition probabilities are decreased. The pressure-broadening effect in molecular spectra is small, and it is unlikely that the radiative lives are appreciably influenced by the presence of other gases.

So far we have considered only electronic transitions. It is also possible to calculate the radiative life for vibrational transitions by making measurements of the absorption in the infra-red corresponding to the vibration-rotation spectrum. Tolman²²⁸ made some calculations on the radiative lives of vibrationally excited molecules of HF and HCl and obtained values for the various individual levels which were mostly of the order of a tenth of a second, but Bourgin³⁰ obtained values about a tenth of those given by Tolman for HCl. It is probable that the radiative lives for vibrational transitions are usually between 10^{-3} sec. and 1 sec. For homonuclear molecules such as O_2 , N_2 and H_2 no vibrational transition is allowed, so that the radiative lifetime will be infinite. The author's approximate calculations of the radiative life for the various vibrations of the CO_2 molecule

* When the equilibrium internuclear distance in the two electronic states is very different, so that there is little overlap between the wave-functions in the two states, the radiative lifetime may be greater. This is probably the case for the red system of CN and the β bands of NO.

† This does not appear to be the case for the violet system of CN, though.

are dealt with in the next chapter. For changes of rotational energy only, the radiative life must be relatively long because of the small value for the frequency ν , and adjustment of rotational energy probably takes place by collision rather than by emission of radiation.

In addition to the determination of radiative lives from measurement of the absorption spectra, more direct determinations have in some cases been made by measuring the decay, with length, of the radiation from canal rays, the velocity of the atoms in the beam being calculated from the temperature. Tolman ²²⁸ says that these results are in general agreement, so far as order of magnitude is concerned, with those obtained from the absorption spectrum.

The Collision Life.

The number of collisions suffered by a molecule of a gas in unit time can be derived by the kinetic theory of gases. A full discussion of such a subject is beyond the scope of this monograph, and the reader is referred to the various textbooks on the Kinetic Theory of Gases. The number of collisions which a molecule suffers per second is equal to

$$4\pi n\sigma^2\sqrt{RT/m}$$

where

n is the number of molecules per cubic centimetre, being equal to Loschmidt's number (2.685×10^{19}) for a gas at N.T.P.

σ is the effective diameter of the molecule.

R is the gas constant $= 1.379 \times 10^{-10}$.

T is the absolute temperature.

m is the mass of the molecule $= M \times 1.66 \times 10^{-24}$ gm., where M is the molecular weight.

The effective diameter of the molecule, σ , is rather difficult to define as it depends on the type of collision. The ordinary kinetic theory values, as derived from measurements of the viscosity, are of the order 4×10^{-8} cm.

Thus a molecule in air at room temperature and pressure makes about 8×10^9 collisions per second, or alternatively, the time between collisions is about 1.3×10^{-10} sec. It will be seen from the expression given above that the number of collisions must be proportional to the gas pressure, and inversely proportional to the square root of the absolute temperature.

The term "collision life" as used throughout this book refers to the mean time taken for an excited molecule to become deactivated by collision, and is often much greater than the time between collisions, as it appears that in many cases the efficiency of the deactivation is small. It is rather difficult to make generalisations or positive statements about the efficiency of collisions in deactivating electronically excited molecules. The transformation of the comparatively large amount of energy held by electronically excited molecules into kinetic energy is unlikely to occur readily on collision, but it seems that activated molecules may react chemically with other suitable molecules with a fairly high efficiency. The marked effect of gas pressure on the quality and quantity of radiation from electric discharges shows that collisions between the molecules are of considerable importance. Thus the effect of oxygen in suppressing the First Positive band system of nitrogen, which has already been commented upon in Chapter II, shows that the deactivation of the excited nitrogen molecules by collision with oxygen molecules is more frequent than deactivation by spontaneous radiation. The number of collisions per second at the pressure of the gases in the discharge tube can only be of the order 10^7 , so that if the excited nitrogen molecules have a radiative life of the order 10^{-6} sec.,* the efficiency of deactivation by collision with oxygen molecules must approach unity. In other cases the collision life may be quite long. Thus active nitrogen produced in electric discharges may continue to glow for a matter of hours if the gases are sufficiently pure, indicating that the activated particles must survive an enormous number of collisions. Although active nitrogen is able to persist for so long if the gases are pure and the walls of the vessel are clean, the introduction of a gas other than oxygen or nitrogen usually results in the molecules of this gas being activated by collision and then radiating themselves; many spectra have been studied using active nitrogen for their excitation.

* The First Positive bands of nitrogen are due to a ${}^3\Pi \rightarrow {}^3\Sigma$ transition, the ${}^3\Pi$ and ${}^3\Sigma$ levels dissociating into ${}^2D + {}^2D$ and ${}^4S + {}^2D$ nitrogen atoms, respectively; since the atomic transition ${}^2D \rightarrow {}^4S$ is not allowed the molecular transition may be regarded as half forbidden, so that the radiative life may be fairly long. The readiness with which the band system appears in discharge tubes indicates, however, that it cannot be so very long, so that the assumption of a value of 10^{-6} is unlikely to be in error by more than a factor of 10.

The best method of arriving at a value of the collision life of an electronically excited molecule is by studying the quenching of the fluorescence. If the pressure of the fluorescing gas is raised, or if another gas is added, the fluorescence is weakened because a proportion of the excited molecules will be deactivated by collision before they have time to radiate. If I_0 is the intensity of the fluorescence at very low pressure, and I the intensity at a pressure p of quenching gas, then

$$I/I_0 = 1/(\tau/t + 1) = 1/(\alpha p + 1)$$

where τ is the radiative life and t is the collision life. This method of studying the quenching of the fluorescence thus gives the ratio of the radiative and collision lives, but a numerical knowledge of the collision life can only be obtained if the radiative life is known, which is seldom the case for molecular energy levels. Baxter¹⁵ measured the quenching of the fluorescence of nitrogen peroxide by NO_2 itself and by other gases. He obtained, for quenching by NO_2 , a value of 50 for the constant α when p was expressed in millimetres of mercury, and concluded that either the effective diameter for collisions was much greater than the gas kinetic value, or the radiative life was abnormally long, being of the order 10^{-5} sec. This latter view was taken by Heil¹¹³, who made some additional measurements on the pressure-broadening of the spectrum lines. It seems that for excited NO_2 molecules the assumption of a radiative life of 10^{-5} sec. and a value of 3×10^{-8} for the collision diameter of the molecule gives an efficiency of one for deactivation by collision; collisions with carbon dioxide, nitrogen or hydrogen are also very efficient in deactivating the excited NO_2 molecules. Orthmann and Pringsheim¹⁰³ examined the quenching of mercury-sensitised fluorescence of thallium by mercury vapour, and found that the thallium lines were still detectable when the pressure of thallium was only 0.01 mm. of mercury, while the mercury-vapour pressure exceeded an atmosphere, from which they concluded that the metastable mercury atoms were able to retain their excitation energy through some 10,000 collisions with other mercury atoms. From these observations it seems that the efficiency of collisions in quenching excited atoms or molecules varies within wide limits.

Persistence of Vibrational Energy.

Although so little is really known about the collision lives of electronically excited molecules, a considerable amount of data is available regarding the life of vibrationally excited molecules. The most general way of obtaining information about the conversion of vibrational energy into kinetic (heat) energy is the study of supersonic dispersion in gases. The velocity of sound in a gas depends on the ratio of the specific heats of the gas at constant volume and constant pressure. The velocity of sound is normally independent of the frequency of the sound, but at high frequencies a step up in the velocity is observed. This is attributed to the failure of the high frequency sound wave to excite the internal vibrations of the molecules before the wave has passed, so that the contribution to the specific heat term made by the vibrations of the molecules drops out. At the frequency corresponding to this step in the curve between velocity and frequency, there is a marked increase in the strength of the absorption of the sound due to the energy of the wave being partly absorbed by exciting the internal vibrations of the molecules during the adiabatic compression as the sound wave approaches, but not being returned to the wave during the final adiabatic expansion. From either the position of the step on the velocity-frequency curve or from this absorption, it is possible to calculate the mean time for the conversion of vibrational energy into thermal energy, this being known as the *relaxation time*. This relaxation time varies over rather a wide range, according to the particular molecular species involved in the collisions, but usually lies between 10^{-5} and 10^{-8} sec. Water appears to be particularly efficient in converting vibrational energy into thermal energy and the measurements of Eucken and Becker^{68 69} show that the relaxation time for pure CO_2 is about 5.7×10^{-6} sec., but is reduced to only 9×10^{-8} sec. by 3% of moisture, the water-vapour molecules being about a thousand times as efficient as the CO_2 molecules in converting the vibrational energy of the latter into heat. In Table 4 the number of collisions with various types of molecule which are required on the average to deactivate a vibrating CO_2 molecule are compared, the data being taken from a paper by Metter¹⁷⁸.

TABLE 4

Diluent	No. collisions required
H ₂ O	60
CO	230
NO	260
N ₂	1,200
pure CO ₂	51,330

In addition to determinations of the relaxation time by supersonic methods, several estimates of the delay in the conversion of vibrational into other forms of energy have been obtained from spectroscopic observations. Dwyer⁵² examined the absorption spectrum of iodine vapour at short time-intervals after the passage of an electric discharge, using a stroboscopic method, and found that the absorption from higher vibrational levels of the iodine molecule was detectable for about $\frac{1}{30}$ sec. after the interruption of the discharge, indicating that iodine molecules raised from the ground state to the first vibrational level were able to persist in this level through several thousand collisions with other iodine molecules. White²⁴⁹ also noted that the absorption spectrum of the CN radical showed bands arising from the $v'' = 1$ level for some 0.003 sec. after the termination of the discharge producing the radicals; this value of the collision life corresponded, at the pressure used for the experiments, to some 10,000 collisions. It has also been shown by Oldenberg and Rieke¹⁹⁰ that for excited OH radicals some 570 collisions were rather inefficient in bringing about thermal equilibrium.

Other methods, such as resonance fluorescence and molecular recombination rates, give information about the transfer of vibrational energy on collision, and the results from these methods are often at variance with the values obtained from supersonic measurements or the more direct spectroscopic method employed by Dwyer. The resonance fluorescence method only gives values for the *transfer* of vibrational energy from *electronically excited* molecules. The recombination method appears to involve three-body collisions, which will have a different probability of producing energy transfer from that for two-body collisions which are responsible for supersonic dispersion and many combustion effects. It is also necessary to distinguish between *transfer* of vibrational energy from one molecule to another of the same species, which probably occurs with relative ease, and *conversion*

of the vibrational energy into other forms such as translational or rotational energy.

The lag in the conversion of vibrational energy into heat energy leads to a lack of equipartition of the energy released by combustion processes, and is of considerable importance in relation to the latent energy and maximum temperatures reached in flames, and especially in relation to afterburning, the author's theory of which is dealt with in the next chapter.

The time taken for the attainment of equipartition of rotational energy with energy in other forms has also received some attention. Oldenberg¹⁸⁸ noticed that the radiation from OH radicals showed an abnormal rotational intensity distribution, indicating presumably that the adjustment of the rotation was slow compared with the emission of the radiation, a time of the order 10^{-6} sec. Lewis and von Elbe¹⁶⁵ have also attributed certain discrepancies between observed and calculated temperatures in explosions to delay in exciting the rotation of the molecules in advance of the flame front. These observations seem at variance with the failure to observe supersonic dispersion corresponding to lag in conversion of rotational energy to and from translational energy. Lewis and von Elbe's results might possibly be explained by assuming that the dissociation of the carbon dioxide molecules is not necessarily the same as that calculated for the temperature of the explosion (see page 124).

Collision-Complexes ; Dissociation of Polyatomic Molecules by Internal Resonance.

Let us consider the collision between two particles which are capable of forming a physically stable molecule. If the particles approach from a distance, then, even though the particles may exert an attractive force on each other, the energy of the system will be such that, unless it is removed in some form or other, the particles will ultimately swing away from each other and become separated. Thus, in order to form a molecule, some of the energy must be removed or absorbed. This can be done either by another particle (three-body collision) or by the surface of the container. It is not, however, necessary to remove the energy completely from the system ; it is sufficient to transform it from the degrees of freedom corresponding to the relative motion of the two particles to some other degree of freedom such

as internal vibration of the newly formed molecule. If this occurs, then a molecule is formed which, since it contains sufficient energy for its own dissociation, is inherently unstable, although it may persist for a short time.

Rosen ²⁰⁸ has given a mathematical treatment of the formation and lifetime of such a collision complex composed of a diatomic molecule and an atom colliding to give a triatomic molecule. He has taken HO_2 , a molecule whose existence is frequently postulated in chain mechanisms for the combustion of hydrogen, as an example, and by making a number of assumptions arrives at estimates of the life of the molecule of the order 5×10^{-15} , 5×10^{-13} , 5×10^{-11} and 2.5×10^{-9} sec., according to whether a certain vibrational quantum number takes the values 1, 2, 3, or 4 respectively. Rice ²⁰⁶ has commented on certain details of the treatment given by Rosen, but agrees in principle. Other mathematical papers on the formation and existence of such collision complexes have been published by Eyring ⁷¹ and Kassel ¹⁴¹.

An experimental demonstration of the existence of at least one such collision complex has been given by Oldenberg and Rieke ^{191a}. In studying the kinetics of the reactions of OH radicals by quantitative measurement of the variation of the absorption with time, they found that the dependence of the rate of removal of the radicals on pressure indicated that three-body collisions were necessary. It was found, however, that the efficiency of the triple collisions was higher than unity if the number of such collisions was computed from gas kinetic data. This was taken to indicate that OH forms collision complexes which have a lifetime much greater than the duration of bimolecular collisions between stable molecules.

In calculating the lifetime of these collision complexes, Rosen assumed that transfer of vibrational energy from one form of vibration of the polyatomic molecule to another form was possible, and that if the molecule possessed sufficient internal vibrational energy for it to dissociate this process of transfer of energy from one form of vibration to another would ultimately lead to the dissociation of the molecule. The probability of this dissociation will be increased if there is any degeneracy in the molecular system, and Rosen quotes the carbon dioxide molecule as an example of a molecule in which such a degeneracy exists; the

possible effect of this degeneracy in producing abnormal dissociation of CO_2 during the combustion of carbon monoxide is discussed later (page 124). It has been suggested by Ubbelohde ²³¹ that the activation energy required before the combustion of hydrocarbons can be initiated depends on the possibility of vibrational energy transfer within the molecule.

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CHAPTER XII

THE AFTERBURNING OF CARBON MONOXIDE

Afterburning.

PHOTOGRAPHS of flame-travel in explosions usually show that the gases behind the flame front continue to glow for some time after the passage of the flame. This is especially true of explosions in closed vessels in which the gases in the centre of the vessel are observed to glow very brightly as the pressure wave travels back through the gases after the explosion. The literature contains numerous reproductions of such photographs showing this after-glow or afterburning, the papers by Bone, Fraser, Winter and Witt ^{20 21} showing some good examples. Apart from the observation of this glow, there is other evidence to show that combustion is not completed by the passage of the flame front. David, Brown and El Din ⁴⁵ have shown, from studies of the maximum pressure reached during explosions of carbon monoxide in closed vessels of various sizes, that combustion is not complete at the moment that maximum pressure is reached. Ellis and Wheeler ⁵⁹ and Ellis and Morgan ⁵⁸ note the afterburning of carbon monoxide and record that the temperature continues to rise after the flame front has passed through the gases, indicating that the combustion processes are not complete. Lewis and von Elbe ¹⁶³ have criticised these papers and conclude that afterburning is not a real phenomenon, but is only a manifestation of the pressure and temperature changes which are bound to occur following an explosion in a closed vessel, and that David, Brown and El Din's results may be due partly to pockets of unburnt gas. It may be noted, however, that David, Leah and Pugh ⁴⁷ have repeated the experiments in a vessel in which pockets of unburnt gas were avoided, and confirm the earlier results. Lewis and von Elbe support their criticism by some experiments on the explosion of mixtures of oxygen and hydrogen. For these oxygen-hydrogen mixtures evidence for the existence of any afterburning is certainly

not conclusive, and for fuels containing hydrogen as well as carbon monoxide the afterburning is at any rate probably of short duration, but for carbon monoxide, which when pure and dry shows a remarkable reluctance to burn quickly or to completion, the existence of some form of afterburning seems to be well established.

The afterburning in the internal combustion engine has been studied by Withrow and Rassweiler and has already been discussed (page 66). Spectroscopic investigation reveals that the afterburning always appears to be due to the combustion of carbon monoxide, the spectrum being identical with that of the moist carbon monoxide flame.

The afterburning is sometimes of considerable duration, and has been observed visually to persist for as long as 14 sec. for explosions of dry carbon monoxide in large closed vessels, although this value is, of course, unusually high. In smaller vessels or in the presence of a trace of moisture or other catalyst the duration is much less, and for fuels other than carbon monoxide is very short.

Latent Energy.

Comparison of observed and calculated maximum temperatures in both explosion and stationary flames often reveals a serious discrepancy. Observations of this difference have mostly been made by David and colleagues, and have been attributed to a "latent energy" of the combustion which is supposed to reside in metastable activated molecules formed during the combustion. The subject has aroused considerable controversy between David and colleagues and Lewis and von Elbe, the difference in opinion depending largely on the choice of the best way of measuring flame temperature, a subject which is briefly dealt with in the next chapter. Again it seems doubtful whether the latent energy is or is not important in the case of ordinary fuels containing hydrogen, but certain that for the combustion of carbon monoxide, either in explosions or stationary flames, the full energy of the combustion process is not immediately liberated.

The latent energy depends considerably on the type of fuel and on the method of combustion, and may range from only 1% of the heat of combustion to as much as 28% in some instances. In closed-vessel explosions it seems that the latent energy is less

for small explosion vessels than for large vessels, and in all cases is highest for carbon monoxide as fuel. As with the afterburning, and indeed most phenomena associated with the combustion of carbon monoxide, the latent energy varies considerably with the dryness of the gas. This is shown by flame-temperature measurements made by David and Pugh⁴⁸ which are reproduced in Table 5. A similar and even greater effect is produced by the

TABLE 5

Water vapour (%)	Flame temperature, ° c.	Latent energy (%)
0	1650	20.5
0.87	1675	19.5
1.50	1690	18.5
2.14	1700	17.5

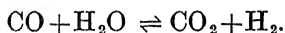
addition of hydrogen to the flame, and the corresponding values for the flame temperature and amount of latent energy are given in Table 6.

TABLE 6

Hydrogen (%)	Flame temperature, ° c.	Latent energy (%)
0	1650	20.5
1	1705	17.5
2	1725	16.5
3	1735	15.5
4	1745	15.0
5	1750	14.5

The Combustion Process ; Vibrationally Activated Molecules.

In the combustion of ordinary fuels containing hydrogen as well as carbon there seems little doubt that the combustion of the carbon monoxide takes place largely through the maintenance of the water-gas equilibrium



The details of the mechanism of the maintenance of the equilibrium may be open to discussion, but the abrupt step in the radiation—hydrogen—pressure curve observed by Garner and colleagues at a critical concentration of hydrogen (see page 97) shows that above a certain concentration of hydrogen the combustion is maintained by the hydrogen, while below this con-

centration the oxidation of the carbon monoxide is direct. The experiments of Bone and colleagues²⁵ on the explosion of intensely dried carbon monoxide with air or oxygen also indicate that with sufficiently powerful ignition pure dry carbon monoxide will combine with oxygen. At high pressure this is especially true, the effect of moisture being relatively unimportant at pressures above 5 atmospheres.

Thus it seems that there must be a mechanism by which carbon monoxide and oxygen can react to form the dioxide. The exact form of this mechanism is doubtful. The various chain mechanisms which have been proposed variously involve atomic oxygen, activated CO_2 molecules, activated oxygen molecules or a peroxide CO_3 . The failure of atomic oxygen to react with carbon monoxide (see page 51) seems to render any mechanism involving these atoms improbable. The reaction may be regarded as simply produced by three-body collisions $2\text{CO} + \text{O}_2$, the molecules being suitably activated thermally, and the existence of an activated complex $\text{CO} \cdot \text{O}_2$ (or CO_3) being postulated if necessary to satisfy the kinetics of the reaction. This is perhaps a little vague, and more knowledge of the initial stages of the combustion would help in a fuller understanding of the whole process, but it will be seen that the initial process is probably less important in determining the rate of the combustion than are the later processes, by which the energy of the combustion is dissipated.

In the chapter on the spectrum of the carbon monoxide flame, it has been pointed out that the normal carbon dioxide molecule, which must be the final product of the combustion irrespective of the mechanism, is not built up from normal carbon monoxide, $\text{CO}(^1\Sigma)$ and normal oxygen, $\text{O}(^3P)$, but from an excited state, probably $\text{CO}(^3II)$. Thus in the formation of carbon dioxide from the monoxide an electronic transition must occur at some stage during the reaction. It seems very unlikely that the carbon monoxide molecules are first activated (that is subjected to the electronic transition) as this would require the very high activation energy of at least 138 k.cal. There is no spectroscopic evidence for the presence of electronically excited carbon monoxide molecules. Hence it may safely be assumed that the carbon dioxide molecules are formed initially in a state which is not the normal electronic state of CO_2 .

It has been suggested by Mulliken that the excited electronic state of carbon dioxide is triangular. It has already been shown that such an assumption would account for the big difference in spectral region between the absorption by carbon dioxide and the emission spectrum observed in the flame. We shall therefore take, as our basic assumption, the fact that the carbon dioxide molecules are formed in an electronically excited state, the shape of which is very different from that of the normal linear symmetrical molecule.

The radiative life of the electronically excited CO_2 molecules is uncertain, but may be as long as 10^{-6} sec. Kondratjew's measurements indicate that one quantum of radiation is emitted for every 125 CO_2 molecules formed; this is a relatively high amount of radiation and clearly shows that the formation of the excited molecules is chemical and not thermal, but if we assume that all the CO_2 molecules are formed in the excited state, then it follows that the collision life of the excited molecules must be much less than the radiative life, being perhaps of the order 10^{-8} sec. It therefore seems that the life of the electronically excited molecules is too short to account for the afterburning. Deactivation of the electronically excited CO_2 molecules by collision may perhaps account for the strong excitation of the OH bands in the spectrum of the flame of moist carbon monoxide.

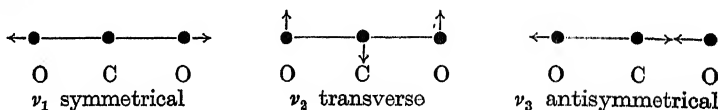
In the electronic transition from the triangular excited state of CO_2 to the linear symmetrical ground state, the sudden change in the equilibrium configuration of the molecule will result in it being left in a very high state of internal vibration. For an electronic transition accompanied by radiation of the excess energy it can be seen from the Franck-Condon principle (page 15) that the transition will occur to high vibrational levels of the ground electronic state. For deactivation by collision the case is rather more complicated, but the fact remains that the equilibrium configuration of the atoms of the CO_2 molecule changes abruptly, and therefore it will probably follow that in this case also the return to the ground electronic state will be accompanied by high vibrational excitation of the CO_2 molecule.

We see, therefore, that the carbon dioxide molecules formed by the combustion of carbon monoxide will be initially in a state of high vibrational energy. That is, they will be vibrationally activated. We now turn to a consideration of the life of these

vibrationally activated CO_2 molecules and to their effect on the combustion phenomena.

Lifetime of Vibrationally Activated Molecules.

It is possible to obtain some information about the radiative and collision lifetimes of vibrating CO_2 molecules from quantitative measurements of the absorption spectrum and from data derived from supersonic dispersion. The CO_2 molecule possesses three fundamental vibrational frequencies which must be considered separately. The three types of vibration are indicated below,



The absorption spectrum of carbon dioxide has been studied by Martin and Barker ¹⁷⁴, who have published curves of the absorption from which rough estimates of the values of the total

absorption $\int \alpha \cdot d\nu$ have been made by the author ⁹⁰. Martin and Barker show curves of deflection (proportional to light intensity) against wave-length for various stated equivalent thicknesses of absorbing gas. These curves were measured up, and, assuming a base line passing through the points of maximum deflection to give the deflection corresponding to light from the source without absorption, a new curve between wave-number and absorption coefficient was plotted. Assuming the ratio of the statistical weights p_1/p_2 as 1 (a value which is unlikely to be in error by more than a factor of two) and that all the molecules were initially in the lowest vibrational state at the temperature of the absorption experiments, the transition probabilities A_{21} were calculated by the formula given by Tolman (see page 100). The several curves for various thicknesses of absorbing gas gave values of A_{21} which decreased somewhat with increasing thickness of gas; this effect was due presumably to the resolving power used for the absorption measurements being barely sufficient, and an approximate extrapolation to zero equivalent thickness of absorbing gas was made. From these values of A_{21} the radiative lives were obtained, assuming in each case that the only possible transition was to the lowest state ($\tau = 1/A_{21}$). The values

obtained are only rough estimates which serve to give an order for the radiative lifetimes, but which cannot be assumed to be numerically accurate on account of the various approximations made and the doubtful adequacy of the resolving power.

For the asymmetrical vibration ν_3 , which corresponds to the 4.4μ band, a value of rather less than a hundredth of a second has been obtained for the average time for the transition from $\nu_3 = 1$ to $\nu_3 = 0$. The lifetime for transitions involving unit decrease in vibrational quantum number for more highly excited molecules (e.g. $\nu_3 = 10$ to $\nu_3 = 9$) may be a little longer, and the total time for radiation of energy stored in the asymmetric vibration, which would mostly be radiated in successive steps in which the vibrational quantum number decreased a unit at a time, might amount to a few tenths of a second at the most.

For the transverse vibration ν_2 corresponding to the absorption band at 14.9μ , a similar calculation gives a radiative lifetime not exceeding 0.2 sec. for the transition $\nu_2 = 1$ to $\nu_2 = 0$.

The symmetrical valence vibration ν_1 is, of course, inactive in the infra-red and does not emit any radiation corresponding to the fundamental frequency itself. Some energy may be lost by radiation of the combination band $\nu_3 + \nu_1$ at 2.8μ . No exact calculation of the lifetime has been made, but it may be assumed that the radiative lifetime for this vibration is relatively long.

A large number of measurements on the dispersion of sound by carbon dioxide are available. The results vary rather widely because of the marked effect of moisture and other impurities in reducing the relaxation time. Examples of this have already been given (page 110). The main sound-absorption peak corresponds to the time-lag in transfer of energy to and from the transverse vibration ν_2 . For pure CO_2 the value of the relaxation time is around 5×10^{-6} sec. at room temperature. Eucken and Nümann⁷⁰ found that the relaxation time decreased slightly at higher temperatures and they gave a value of 2.0×10^{-6} sec. at 673°K . compared with 7.0×10^{-6} sec. at 293°K . The relaxation time corresponds to transitions between $\nu_2 = 1$ and $\nu_2 = 0$, and the time lag for vibrational energy transfer at higher temperatures and for more highly excited molecules may be rather different; the vibrational energy will not be transferred at a single collision but in successive small steps, the highly excited molecules probably losing some of their excess energy fairly

quickly, but with the later steps taking a time similar to that given by the supersonic determinations. Assuming that the relaxation time at high temperature is of the order 10^{-6} sec., then the time for the vibrationally activated molecules to reach equipartition of energy with other forms may be about 10^{-5} sec. for the transverse vibration, and less by a factor of the order of 100 in the presence of a few per cent. of water vapour.

The symmetrical valence vibration ν_1 , having a higher frequency than ν_2 , contributes less to the specific heat of the gas and has a less marked effect on the sound absorption and dispersion. On classical grounds the symmetrical vibration would be expected to transfer its energy by collision much less readily than does the transverse vibration, but Eucken and Nümann⁷⁰ have expressed the opinion that the symmetrical vibration is excited as easily as the transverse vibration, not because of equality of sensitiveness to impact but because of the very rapid adjustment of equilibrium of the energy in the two forms of vibration (see also next section on dissociation). Recently Pielemeier, Saxton and Telfair¹⁹⁹ have observed a shelf on the sound-absorption—frequency curve which they interpret as corresponding to ν_1 , the relaxation time for which may therefore be a little longer than for ν_2 . It also appears that the transfer of energy from this form of vibration is rather less dependent on the presence of moisture.

The asymmetrical valence vibration ν_3 has such a high frequency that it contributes very little to the specific heat at room temperature and does not therefore produce absorption or dispersion of sound. The collision lifetime of this vibration should be longer than for the transverse vibration.

We may now compare the radiative and collision lives of CO_2 molecules for the three types of vibration.

The transverse vibration ν_2 has a collision life of the order 10^{-6} sec. against a radiative lifetime of rather less than 0.2 sec. Thus energy initially stored in this form of vibration will be transferred to other degrees of freedom by collision before there is time for any appreciable radiation of the characteristic band at 14.9μ . This explains the failure of Garner and Johnson and others (page 90) to observe this radiation from the flame, a result which at first sight seemed rather surprising.

For the asymmetrical vibration ν_3 the radiative lifetime has

been calculated to be rather less than 0.01 sec.; we have no independent knowledge of the collision lifetime, but it is known from the work of Garner and colleagues that a flame of carefully dried carbon monoxide does radiate the infra-red band at 4.4μ very strongly, the total radiation being sometimes as much as 24% of the heat of combustion. Thus, experimentally, the collision life, in pure CO_2 , must be at least comparable with the radiative lifetime. Also from Garner's work we know that the radiation at 4.4μ is very much less if the gas is moist or if other catalyst is added. Thus it may be assumed that, for this vibration also, the relaxation time (collision life) is greatly reduced by the presence of moisture and so the vibrational energy is lost by collision with water molecules rather than by radiation.

The symmetrical vibration ν_1 has a relaxation time of around 10^{-5} sec., and since this vibration is inactive in the infra-red the energy is, of course, lost principally by collision (perhaps after transfer to the transverse form of vibration). The combination band $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_2$ at 2.8μ does emit some radiation and it is interesting to note that Garner and Johnson found that this band was less sensitive to the presence of water than the other band; this may be linked with the less marked effect of moisture on the relaxation time for ν_1 recorded by Pielemeier, Saxton and Telfair.

The above deductions may be summarised as follows. For the combustion of pure dry carbon monoxide the energy stored in the asymmetrical vibration is lost mostly by radiation in a time of not more than a few tenths of a second, while the energy in the other two vibrations will reach equipartition with the energy in other degrees of freedom (heat energy) in a time of the order 10^{-4} sec. In the presence of moisture or other catalyst the vibrational energy of all forms will mostly be lost by collision with water or catalyst molecules and transformed into heat in a very much shorter time.

Abnormal Dissociation.

We have seen that the newly formed CO_2 molecules will be vibrationally activated and that this excess vibrational energy may persist for an appreciable fraction of a second before equipartition with the energy in other degrees of freedom is established. There is reason to believe that this temporary lack of equi-

partition of the energy may lead to abnormally high dissociation of the CO_2 molecules^{90 91}.

In equilibrium the percentage of dissociation of carbon dioxide into the monoxide and oxygen will be determined by the temperature. It is the internal vibrational energy of the molecules which governs the amount of dissociation, and it is clear that if the molecules are vibrationally activated, that is if their effective vibrational temperature exceeds the measured temperature, which is determined chiefly by the translational energy of the molecules, the amount of dissociation will correspond to that for the effective vibrational temperature and not to the measured temperature. Thus, although the temperature of the gas as recorded by some normal method may be, say, 2000°C ., at which temperature the dissociation of carbon dioxide would be small, the effective vibrational temperature may be very much higher and the equilibrium value of the amount of dissociation at this very high effective temperature will be considerably greater.

For carbon dioxide there is a degeneracy between some of the vibrational energy levels owing to the almost perfect equality $\nu_1 = 2\nu_2$ which has been discussed by Dennison⁵⁰ in his analysis of the infra-red spectrum. As pointed out by Rosen (see page 113), this may result in rapid transfer of vibrational energy from one form of vibration to the other. We have seen in discussing the formation of collision complexes that such a degeneracy as does in fact occur for CO_2 will favour a high rate of dissociation if the molecule contains sufficient vibrational energy. It is unlikely that the newly formed CO_2 molecules would be endowed with sufficient vibrational energy to result in their own dissociation, but collisions with other similarly activated molecules might result in individual molecules being dissociated during the later stages of the combustion process.

Recently, since the author's papers on the subject were communicated for publication, direct experimental evidence for such abnormal dissociation in explosion flames of carbon monoxide burning in air or oxygen has been obtained by David, Leah and Pugh⁴⁷. In these experiments the temperatures for various mixture strengths were measured, using a bare platinum-rhodium wire and a similar wire coated with quartz. It was found that for rich mixtures, containing excess of carbon monoxide, the temperatures recorded by the two wires were not very different,

but that for weak mixtures containing excess of oxygen the quartz-coated wire recorded a very much lower temperature, as is shown by the curves reproduced in Figure 8, in which T_p and T_q are the temperatures recorded by the bare platinum-rhodium thermometer and the quartz-covered one, respectively. The big difference, which in some cases amounts to over 300°C. , is attributed to there being a large amount of dissociation in the gases, the quartz-covered wire recording the actual temperature, while the uncovered wire records a higher temperature owing to recombina-

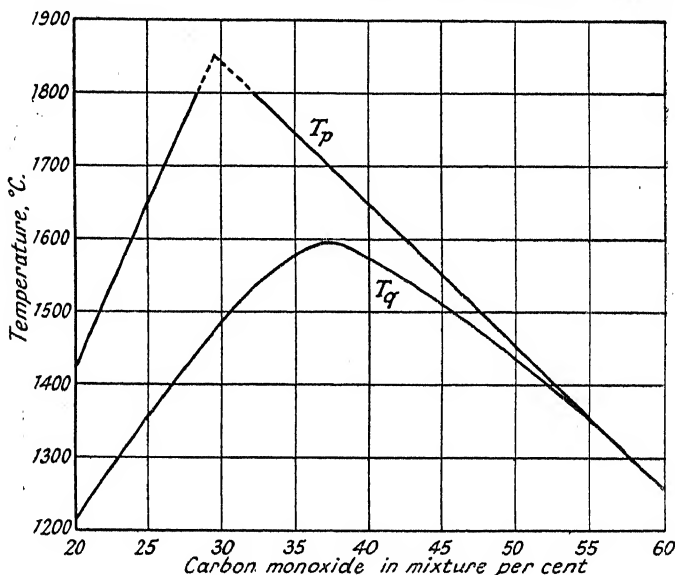


FIG. 8.

tion of the dissociated molecules on the metal surface. Excess of carbon monoxide suppresses the dissociation, showing that although the amount of dissociation is quite abnormal, some form of equilibrium is still maintained.

We have seen that the presence of a catalyst such as moisture hastens the re-establishment of thermal equilibrium by deactivating the vibrating molecules by collision, and it is therefore to be expected that the amount of dissociation will be less abnormal for combustion in the presence of moisture or hydrogen. Thus for ordinary fuels the effect will be much less marked. In estimating the amount of dissociation it must be remembered that

sampling of exhaust gases will be unlikely to reveal the true composition of the mixture at the moment of leaving the engine as the rapid adjustment of the equilibrium will reduce the amount of dissociation as the sample is collected ; to freeze out at the equilibrium existing in the engine requires very rapid cooling, but the introduction of any metal surfaces to effect the cooling will tend to restore the equilibrium to that for normal thermal distribution of the energy.

Discussion.

It is now proposed to give a brief summary of the main points of the theory of the later stages of the combustion of carbon monoxide, and then to discuss how the theory explains the various peculiarities of the combustion, with especial reference to the afterburning and the effect of moisture on the combustion and infra-red spectrum.

The main steps in the theory are as follows :

(a) In the formation of carbon dioxide from carbon monoxide an electronic transition must take place at some stage during the combustion.

(b) This transition is most likely to occur after the formation of the CO_2 molecule and not as activation of the CO .

(c) The difference in region of the absorption and emission spectrum of CO_2 indicates that the shape of the molecule in the normal and excited electronic states is very different.

(d) Hence the electronic transition will result in the newly formed CO_2 molecules being in a high state of internal vibration.

(e) In the pure gas this vibrational energy will persist for an appreciable fraction of a second.

(f) In the presence of moisture or other catalyst the vibrating molecules will be quickly deactivated by collision with water or catalyst molecules.

(g) The high effective vibrational temperature of the newly formed molecules will result in abnormally high dissociation, this being assisted by a degeneracy in the vibrational levels for CO_2 .

(h) The presence of moisture or other catalyst will, by deactivating the vibrating molecules, quickly restore thermal equilibrium and so reduce the amount of abnormal dissociation.

The afterburning and latent energy can readily be explained in terms of this abnormal dissociation, for although the life of

the vibrationally activated molecules themselves is probably less than a second the successive dissociation and recombination of the molecules will prolong the combustion process. The spectrum of the afterburning is, of course, the same as that of the flame itself, as is to be expected if it is due to recombination following dissociation. The increase in brightness of the afterburning in closed vessels as the pressure wave travels back through the gases is due to the increase of pressure shifting the dissociation equilibrium and so forcing the combination of more carbon monoxide with oxygen.

The afterburning and the afterglow of carbon dioxide in a discharge tube (Fowler and Gaydon⁷⁵) have in the past been ascribed by David and colleagues to emission of light by activated (metastable) molecules of carbon dioxide, although Egerton and Ubbelohde⁵⁵ have pointed out certain objections to this. It is now clear that the activated molecules, being vibrationally activated and not electronically activated, could not emit radiation in the ultra-violet identical with the normal flame spectrum. The emission from the activated molecules lies in the infra-red as shown by Garner and is of considerable amount. The visible and ultra-violet emission from both the afterburning and the afterglow is due to recombination following dissociation, and this recombination is accompanied by the emission of the usual flame spectrum.

The strong infra-red radiation from explosions of dry mixtures agrees with the long life of the vibrationally excited molecules under such conditions, this allowing more time for radiation. The large amount of energy radiated (up to 24% of the total heat of combustion) indicates that the amount of vibrational energy stored in the newly formed molecules is very high. The failure of various observers to obtain the $14.9\ \mu$ band in emission from the flame is due to the long radiative life and short collision life of the molecule for this form of vibration. The failure to observe this band is incidentally clear proof that the emission should be regarded as due to chemical rather than thermal causes, as, if the excitation was thermal, the number of molecules excited and deactivated by collision would be the same, and so the population of vibrationally excited molecules would be maintained and so enable emission of the $14.9\ \mu$ band.

If it is assumed that the combustion process is largely thermal

in nature for relatively dry mixtures, then the loss of energy by radiation and by storage in the vibrationally activated molecules and the high abnormal dissociation will result in there being much less energy available for the maintenance of the combustion. This explains the reduction in flame speed on drying, and also the low percentage combustion for such mixtures. The presence of moisture transforms the vibrational energy of the newly formed molecules into thermal energy very quickly and so sets the heat of combustion free to maintain the combustion process.

This theory of the afterburning and other peculiarities of the combustion is not, of course, entirely new. Garner, Hall and Harvey⁸¹ have been led to conclude, from their observations on the infra-red spectrum, that

During the combustion of the dry hydrogen-free gases, the product, carbon dioxide molecules, contains a large fraction of the energy of combustion. This forms at least 24% of the total energy set free. These molecules are very stable towards collisions, but can lose their energy by the emission of radiation or by resonance to other molecules of carbon dioxide. As a result of resonance, the activated molecules possess an apparently long duration of life. Since their internal energy is only slowly converted into kinetic energy, the loss of energy to the walls occurs very largely by Brownian movement of activated molecules.

On the introduction of small percentages of hydrogen, the average duration of life of the activated molecules decreases, and the rate of conversion of internal into kinetic energy increases. Thus, the temperature and speed of flame are augmented, and at the same time, there is an increase in the loss of energy from the flame by thermal conductivity.

When higher percentages of hydrogen are added, discontinuities appear on the radiation-pressure curves, which can only be explained as due to changes in the mechanism of the reaction, and the suggestion that the afterburning might be due to internal vibrational energy of the molecules has also been discussed, but the suggestion had been rejected (David and Davies⁴⁶) because this would not account for the long duration of the afterburning. The semi-quantitative treatment given by the author, and the realisation of the cause of the abnormal dissociation, which is responsible for the afterburning, does, however, seem to put the whole question of the afterburning and peculiarities of the combustion of carbon monoxide on a firmer footing. The author is indebted to Professor Egerton for his interest and suggestions on the many varied aspects of this afterburning problem.

CHAPTER XIII

FLAME TEMPERATURES, MEASURED AND CALCULATED

Flame Temperature?

THE measurement of the temperature of a flame is one of the least satisfactory of physical measurements. This is partly due to experimental difficulties and partly because of the difficulty in defining the temperature of a flame. During the combustion process a large amount of energy is liberated and this energy may momentarily take many forms, and the energy will not in general be equally partitioned among these various forms. We have seen in previous chapters that molecules may be formed which are in a state of intense internal vibration. It is also at least conceivable that molecules which are formed by decomposition or collision processes may initially possess abnormal rotational or translational energy. Flames also contain many chemically reactive bodies such as the radicals OH and CH, and these may react chemically at any surface which is introduced into the flame, and so liberate energy at this surface and raise its temperature above that of the flame gases. Thus the temperature taken up by a thermometer introduced into the flame may differ considerably from that of the flame gases. The flame temperature itself may have at least three possible values corresponding to the effective rotational, vibrational and translational temperatures of the molecules. Moreover, until equilibrium is reached it is possible that different types of gas molecule may have different effective temperatures; thus perhaps CO_2 molecules might on the average possess an excess of vibrational energy, while OH radicals might possess initially an excess of rotational energy, while, say, sodium atoms in the flame formed by decomposition of sodium chloride might be endowed with excess kinetic energy until this is lost by collision.

With all the normal methods of determining temperature, such

as the use of thermocouples, platinum thermometers or optical pyrometers, these difficulties in assessing the likely effect of collisions of the various gas molecules with the surface of the thermometer render the values obtained of doubtful reliability. Unless especial precautions are taken the correction for loss of energy by radiation is also rather uncertain. With fast-moving gases, such as engine exhaust gases, it is also necessary to make a correction for the adiabatic heating of the thermometer, and this may introduce difficulties if the gas flow is not uniform. Thus some investigators have been led to use the spectral line reversal method for determining flame temperature. As this method does not require the introduction of any solid body into the flame it is free from many of the difficulties encountered in ordinary thermometry.

Spectroscopic Methods of Measuring Flame Temperature.

If a metal, such as sodium, whose resonance line lies in a convenient region of the spectrum, is introduced into a flame, then the resonance line will appear in emission in the spectrum of the flame. If, however, light from an incandescent body which is hotter than the flame is allowed to pass through the flame, the spectrum of this light will show the resonance line reversed, that is, the resonance line will appear in absorption. It has been shown that, provided the luminescence from the flame itself is negligible and the emissive power of the flame for the wavelength of the metallic line emitted is equal to unity, the line will appear reversed against the continuous emission from the incandescent body if this body is hotter than the flame, but will be observed in emission as a bright line superposed on the continuum if the flame is the hotter, while when the incandescent body and the flame are at the same temperature the line will not be observed at all, being of the same intensity as the continuous spectrum.

This provides the basis of the spectral line reversal method of determining flame temperature. A suitable metal vapour, usually sodium, although lithium and thallium have been tried, is introduced into the flame by spraying in an aqueous solution of a salt such as sodium chloride, and the spectrum of an electrically heated black body is viewed through the flame. By adjusting the temperature of the black body until the metallic line is neither seen in emission nor absorption and measuring this

temperature of the black body, the flame temperature may be determined. The method was first used by Kurlbaum, and shortly afterwards by Fery, and of recent years a number of investigators have used the spectral line reversal method for determining the temperature of various flames, e.g. Griffiths and Awbery¹⁰⁵, Loomis and Perrott¹⁶⁸, Jones, Lewis, Friauf and Perrott¹³⁸.

The method, although convenient and free from many of the difficulties and objections to normal methods of thermometry, has not escaped without criticism, especially by David^{41, 44}. Even Jones, Lewis, Friauf and Perrott admit that a colour correction is necessary and that the lithium red line gave less satisfactory results than the sodium lines, and that with thallium no true reversal of the line could be obtained. Apart from the possibility that the basic conditions stated above may not be satisfied, and the chance that the metal atoms are not in thermal equilibrium with the flame gases,* it seems that there must be a tendency for the method to give a value for the temperature of the outer sheath of the flame, rather than of the body of the flame, although Griffiths and Awbery's comparison of the temperatures obtained from the reversal of the sodium line with values obtained by a hot-wire method do not indicate this.

It is also possible, in theory, to obtain flame temperatures from observation of the rotational intensity distribution of a band system which is emitted by the flame, such as the bands of CH or OH. Such observations as have been made by this method indicate abnormal temperatures. This shows that the electronically excited molecules emitting the band system are not in thermal equilibrium, the value of the effective rotational temperature obtained by this method bearing little relation to the true flame temperature. It is possible that the introduction into the flame of a vapour which possesses absorption bands in a convenient spectral region, such as bromine or iodine vapour, might enable the temperature of these molecules to be determined by quantitative measurements of their absorption spectra. The method would be free from many of the objections raised against

* It has recently been shown by Magee and Ri¹⁷¹ that sodium atoms may be excited by the reaction $\text{Na} + 2\text{H} = \text{Na}^* + \text{H}_2$. This chemiluminescence might well cause the sodium radiation to be of a non-thermal character.

other forms of thermometry but would require very high resolving power, so that it could only be used in laboratories equipped with large grating spectrographs, and the calculation of the results would be tedious.

Specific Heats ; Calculated Flame Temperatures.

The calculation of theoretical maximum flame temperatures requires, of course, a knowledge of the specific heats at high temperatures of the various constituent gases. The practical determination of specific heats at high temperatures is far from straightforward, and although much work has been done on the subject most of the results must be viewed with suspicion because of the difficulty in temperature measurement already discussed and the uncertainty about the amount of dissociation and delay in equipartition of energy during the explosions used in most methods to reach the highest gas temperatures. Specific heats can, however, be calculated theoretically from spectroscopically determined data, and David ⁴² has advocated the use of these very accurate theoretical values, in preference to doubtful experimental values, for use in combustion work. Such values based on spectroscopically determined molecular constants are now in fairly general use for calculating flame temperatures and drawing up heat balance equations.

The calculation of specific heats and other thermodynamic quantities falls within the scope of a book on thermodynamics rather than on the subject of this monograph. It may be said briefly that in thermal equilibrium the energy is, classically, partitioned equally among the various possible degrees of freedom. An ordinary molecule may possess energy of translation (three degrees of freedom), rotation and vibration, and possibly of electronic excitation. At ordinary and high temperatures the translational and rotational degrees of freedom of the molecules are fully excited, but this is not necessarily the case with the vibrational and electronic degrees of freedom. For stable molecules the amount of energy will, as explained in the first chapter, be quantised. According to the Boltzmann distribution law the number of molecules with a given energy E is proportional to

$$e^{-E/kT}$$

where k is the gas constant per molecule and T is the absolute temperature. Since the vibrational energy is quantised, E can only take certain definite values, and as the vibrational frequency is fairly high for most molecules, it follows that at room temperature nearly all the molecules must be in the lowest vibrational state, and it is only at high temperatures that an appreciable number of molecules are excited to higher states of vibrational energy. Thus at room temperature the vibrational degrees of freedom will not contribute materially to the specific heat of the gas, but at higher temperatures these vibrational degrees of freedom will become of increasing importance and the specific heat will be greater. From the Boltzmann distribution law it is possible, in equilibrium, to predict the proportion of molecules in any given energy state, so that if all these energy states are known from spectroscopic data it becomes possible to determine the variation of the energy content of the gas with temperature, that is the specific heat.

For such a determination of the specific heats at various temperatures it is necessary to know the vibrational energy levels of the particular molecular species. These vibrational energy levels can, for a diatomic molecule, be determined in most cases quite easily from the analysis of any band spectrum involving the ground electronic state. For polyatomic molecules the analysis of band systems corresponding to electronic transitions is difficult, and it is usual to determine the values of the various vibrational frequencies from observations of the infra-red absorption spectrum and the Raman spectrum.

The electronic energy levels are usually so high above the ground electronic state that even at the highest temperatures encountered in combustion work the contribution made to the specific heat by variation of the electronic energy of molecules is negligible. In a few cases, however, low-lying electronic energy levels contribute a little to the specific heat. The $^1\Delta$ level of oxygen is an example of this.

The author has made no attempt to comb the literature for the numerous determinations of specific heats of gases at high temperatures. The method of calculating various thermodynamic quantities from spectroscopic data has been given by Lewis and von Elbe ¹⁶⁴. Reviews summarising some of the work up to 1934 have been published by Zeise ²⁵⁶ who has also made calcula-

tions directly designed for use in combustion work ^{257 258}. Papers giving values for the specific heats and other thermodynamic quantities at high temperatures for O_2 , N_2 , H_2 , CO , CO_2 , H_2O , etc., have also been noted ^{100 101 136 137 140}.

Differences between observed and calculated flame temperatures are sometimes encountered. Much of this work has already been discussed in the sections on the latent energy and afterburning of carbon monoxide. The differences are largely due to the lag in equipartition of vibrational energy. This lag in the equipartition of energy, of which evidence is obtained spectroscopically and from supersonic dispersion, can also produce deviations of actual from calculated flame temperatures in another way. If inactive diluents such as nitrogen are slow to acquire vibrational energy the specific heats of these diluents will, during the early stages of an explosion, approximate more to the low temperature values than to the high temperature values when the vibrational degrees of freedom are excited. Thus the actual temperature of the flame, determined in terms of the average translational energy of the molecules, may exceed the value calculated using equilibrium values for the specific heats. Lewis and von Elbe ¹⁶⁴ have drawn attention to this possibility, and have also ¹⁶⁵ suggested that even the rotational energy of the molecules may require some appreciable time interval for their excitation.

CHAPTER XIV

DISSOCIATION ENERGIES

Heats of Formation.

IN drawing up chemical equations to represent combustion processes an exact knowledge of the amount of energy absorbed or set free during the reaction is necessary for a full understanding of the likelihood of the reaction taking place under any given conditions. When the equation represents a reaction between stable chemicals to give stable products it is usually possible to measure experimentally the amount of heat liberated or absorbed. For very many of the chemical reactions taking place during combustion, the reactants are not, however, stable chemicals which can be isolated. This is particularly true for many of the chain mechanisms which have been postulated, these involving either chemically active radicals, such as OH, or free atoms. Although the heat of formation of these radicals, or the amount of energy required to dissociate molecules into free atoms cannot readily be determined by direct chemical measurement, it is frequently possible to calculate these quantities with considerable accuracy from spectroscopic data. Fortunately it is just the diatomic molecules, which are the most difficult to treat chemically, for which spectroscopically determined dissociation energies are most often available.

If, for a polyatomic molecule, the heat of its formation from simpler molecules can be determined experimentally, and if the heats of dissociation of these simpler molecules are known from spectroscopic data (or otherwise), then the atomic heat of formation of the polyatomic molecule can be calculated. The atomic heat of formation of a molecule is the energy required to split it up completely into its constituent atoms. If the atomic heats of formation of all the substances entering into a chemical reaction are known, then the heat of the reaction can be obtained directly as the difference of the sum of the atomic heats of formation of the initial and final substances present. Hitherto uncertainty

about the heat of sublimation of solid carbon has led to some difficulties, but it will be shown below that this can be determined from a knowledge of the heat of dissociation of either carbon monoxide or the cyanogen radical.

The calculation of the heat of dissociation of a diatomic molecule from spectroscopic data may be resolved into two problems, the determination of a dissociation limit, either directly or by observation of a predissociation, and the determination of the dissociation products.

Dissociation Limits.

If the vibrational energy of a diatomic molecule is increased the amplitude of vibration will increase and for a certain definite value of the vibrational energy the amplitude will become infinite, that is the two atoms of the molecule will swing apart and will not return; this corresponds, of course, to dissociation of the molecule. On page 14 some typical potential energy curves were sketched out, and the vibrational energy levels were shown to close up as the dissociation limit was approached. The energy required to dissociate the molecule is equal to the difference in energy between that at the limit to which the vibrational levels converge and that for the lowest vibrational level, $v'' = 0$.

If it were possible, by observation of a band spectrum, to determine all the vibrational intervals for the lowest electronic state, then by summing these intervals the dissociation energy could be found directly. It is not, however, possible to observe transitions from the highest vibrational levels, and so it becomes necessary to make an extrapolation to the convergence limit, using those vibrational levels which are known. The accuracy of the extrapolated value depends on how many levels are known from experimental data and, to some extent, on the method of extrapolation. It was stated (page 7) that the vibrational energy levels of a molecule can be represented by the formula

$$E = E_e + v \cdot \omega_e + v^2 \cdot x_e \omega_e + \text{etc.}$$

If the higher terms were negligible, then it can readily be shown that the levels would converge to a limit such that the dissociation energy would take the value

$$\omega_e^2 / 4x_e \omega_e - \frac{1}{2} \omega_e,$$

and Birge and Sponer¹⁸ used this method of extrapolation to evaluate the dissociation energies of a number of molecules. The method usually gives values which are rather too high, and Birge¹⁷ has since shown that there is often a discontinuity in the curve between the vibrational energy and the vibrational quantum number which renders any form of extrapolation rather uncertain. The simple method of plotting the known vibrational energy intervals against vibrational quantum number and extrapolating the curve by hand to zero interval and then taking the total area below the curve as representing the dissociation energy is probably as accurate as most methods; it is then at least easy to estimate by how much the value obtained may be in error, whereas more involved mathematical extrapolations tend to obscure an estimate of the probable error. As has been said, the accuracy of the value of the dissociation energy determined by summing the vibrational energy intervals depends greatly on the number of such intervals known from the analysis of the band spectrum. In some cases where a large number of intervals is known the method gives values which are reliable to at least 10%, but in cases where only a very few vibrational energy intervals are known, the value obtained should be treated with reserve, although even in such cases it is often of use in fixing the dissociation products if an alternative method, such as predissociation, gives a more accurate value for a dissociation limit, but the products of the dissociation are uncertain.

For some molecules, such as Cl_2 and O_2 , it is possible to observe absorption bands, corresponding to transitions from the lower vibrational levels of the ground electronic state to vibrational levels of an excited electronic state, which converge right up to the dissociation limit for this excited state, and beyond to the continuous absorption corresponding to photo-dissociation. In Fig. 9a two potential energy curves with the usual vibrational energy levels drawn in, in the conventional way, are shown. The vertical line AB corresponds to absorption from a vibrational level of the ground state to a normal quantised vibrational level of the upper state and will be represented by a band in the absorption spectrum. The line CD, on the other hand, corresponds to a transition to the dissociated molecule, and since the energy of the dissociated molecule is not quantised (because the atoms will fly apart with kinetic energy equivalent to the excess

of energy over the dissociation energy) the absorption spectrum in this region will be continuous and not banded.

By observing such an absorption system showing the convergence of bands to a limit, followed by continuous absorption, a very accurate value for the dissociation energy of the molecule in the excited electronic state can be obtained. This value, D_2 , will not in general be the same as the normal dissociation energy of the molecule, D_1 , as the products of the dissociation of the excited molecule may not be normal atoms, one or both of them

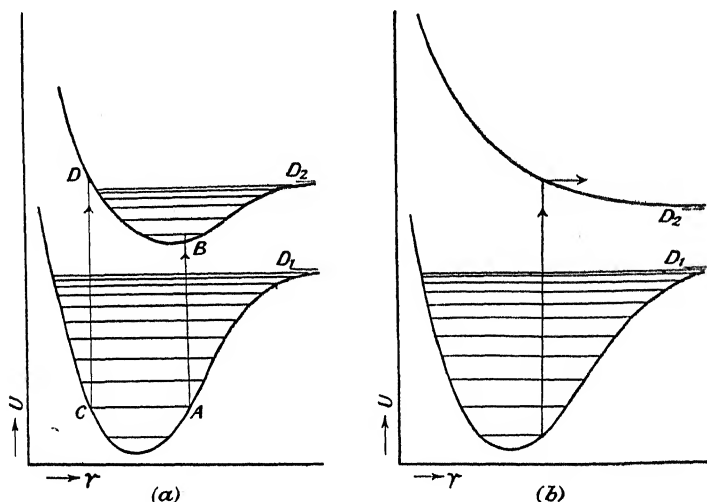


FIG. 9.

being excited. The difference between D_2 and D_1 must correspond to a possible energy difference in the states of one of the atoms (or the sum of such differences for both atoms), and thus frequently is equal to the energy corresponding to a spectrum line of one of the atoms. The dissociation limit D_2 will most frequently lie above D_1 , but if the products are the same D_1 and D_2 will coincide, while in some cases D_2 may lie below D_1 .

As an example of this method of determining the dissociation energy, the Schumann-Runge bands of oxygen correspond to absorption from the ground $X^3\Sigma_g^-$ state to the $B^3\Sigma_u^-$ state and show bands converging to a continuum in such a position that the $B^3\Sigma_u^-$ state is found to have a dissociation limit at 7.049 electron-volts. It will be shown later that the ground $X^3\Sigma_g^-$

state dissociates into two normal oxygen atoms in 3P states, while the excited $B^3\Sigma_u^-$ level dissociates into a normal 3P oxygen atom and an excited 1D atom. It is known from the analysis of the atomic spectrum of oxygen that the transition 1D to 3P would correspond to 1.967 e.v., so that the energy of dissociation of the normal state of oxygen is $7.049 - 1.967 = 5.082$ e.v. = 117.2 k.cal./mol.

If the upper electronic state of a molecule is unstable, that is the potential energy curve does not show a minimum but only an increase of potential energy corresponding to the repulsive force between the atoms as they are brought together, then the absorption spectrum will be continuous. The long-wave limit of this continuous absorption will then correspond to a value for a dissociation energy of the molecule, provided the absorbing gas is cool so that absorption only takes place from molecules in the lowest vibrational state. This is indicated in Fig. 9b. The dissociation limit D_2 may again be above, below or coincident with the dissociation energy D_1 for the normal molecule. The long-wave limit of such an absorption continuum is seldom sharp, and in some cases the observed end of the continuum may lie to considerably shorter wave-lengths than that corresponding to the true limit. It is, however, possible, in some cases, such as the alkali-metal halides, to obtain reasonably accurate values of the dissociation energy by this method, and wherever such continuous absorption is observed it is possible to give an upper limit to the value of the dissociation energy.

In some cases, when the continuous absorption corresponds to dissociation into a normal and an excited atom, an atomic line is emitted by fluorescence. The long-wave limit at which this atomic fluorescence is excited gives the dissociation limit, and the dissociation products can in this case be determined directly, as the molecule must dissociate into the excited atoms giving the fluorescence.

Predissociation.

In some cases the sharp lines of a branch of a band, due to the rotational fine structure, are found to terminate abruptly, the last line or two of the branch being diffuse and then the branch coming suddenly to an end. This is known as predissociation and takes place when the energy content of the molecule

exceeds that for dissociation, and a radiationless transition to the dissociated condition is possible. There are several ways in which a predissociation may be caused, and these are discussed in most textbooks on molecular spectra. The most frequent cause of predissociation in diatomic molecules is overlapping of the discrete rotational and vibrational energy levels of a stable excited electronic state by a dissociation continuum belonging to another electronic state. The radiationless transition to this state can only occur if a number of selection rules are obeyed. Thus the quantum number Λ (see page 12) may only change by 0 or ± 1 , while S must be the same for both states, and so on. These selection rules greatly reduce the number of conceivably possible predissociations which occur, so that in practice band systems involving electronic energy levels far above the dissociation limit of the ground state are frequently observed. From a knowledge of the various selection rules, which have been derived mathematically from perturbation theory, it is usually possible to decide into which electronic state the predissociation takes place.

If predissociation occurs above a certain energy value, then it follows at once that there must be a dissociation limit below this value. When a predissociation is observed it is often possible to fix the dissociation limit within a very narrow range of values. This can be done from a knowledge of the potential energy curves in the various electronic states and by taking into account the various selection rules for the predissociation; a treatment of the subject is beyond the scope of this monograph and the reader is again referred to books dealing with the more advanced theory of molecular spectra.

The radical CH shows a well marked predissociation, and this may be seen in the reproduction (Plate 2*d*) of the spectrum of an acetylene flame taken with long exposure on a photographic plate of high contrast. This shows the P branches of the (1, 0) and (1, 1) bands of the 3900 Å. system becoming suddenly diffuse and ending abruptly at P(11) in each case, as indicated by the arrows. This predissociation in the 3900 band of CH was first reported by Shidei²¹⁷, who calculated the dissociation energy, this value being subsequently corrected (because Shidei had apparently included the vibrational energy of the lowest vibrational state in his value) by Herzberg¹²³ to 3.47 e.v. = 80.0 k.cal./mol. Gerö

and Schmid⁹⁶ have recently observed predissociation in the 3143 Å. band of CH as well. Other molecules of interest to the theory of combustion whose dissociation energies have been determined with the aid of predissociation phenomena are H₂, N₂, NO and CO.

Dissociation Products.

Although it is frequently possible to determine an accurate value for a dissociation limit, it does not always follow that it is possible to determine without ambiguity the dissociation energy for the splitting into normal atoms. It is first necessary to determine the products, that is the degree of excitation of the atoms, corresponding to the known limit. If, as is usually the case with diatomic molecules, the type of the electronic state suffering the dissociation is known, then the *Wigner-Witmer correlation rules* are frequently of assistance in determining the products, or at any rate in reducing the number of possibilities.

Wigner and Witmer²⁵¹ have derived mathematically certain rules for determining what types of molecular state may result from combining atoms in various types of electronic state. These rules are discussed and tabulated in the original paper and by Mulliken¹⁸² and Herzberg¹²³. For two atoms with spins S_1 and S_2 (multiplicities $2S_1+1$ and $2S_2+1$) the molecule resulting from their combination may have a spin S given by

$$S = (S_1+S_2), (S_1+S_2-1), (S_1+S_2-2), \dots, (S_1-S_2)$$

so that, for example, a combination between atoms in triplet ($S_1=1$) and doublet ($S_2=\frac{1}{2}$) states could result in a molecule in a quartet ($S=1\frac{1}{2}$) or a doublet ($S=\frac{1}{2}$) state. For two atoms with orbital angular momenta defined by the quantum numbers L_1 and L_2 the corresponding molecular quantum number A may take the values

$$A = (L_1+L_2), (L_1+L_2-1), \dots, 0.$$

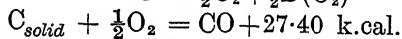
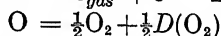
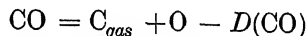
Thus, for example, an atom in a D state ($L_1=2$) combining with an atom in an S state might form a molecule in a A ($A=2$), Π ($A=1$) or Σ ($A=0$) state. Rules for determining whether the molecular state is $+$ or $-$, and whether it is even (g) or odd (u) in the case of homonuclear molecules, have also been derived and the results tabulated.

As an example of the application of these rules we may take

the case of the dissociation of oxygen, which has already been referred to. Observations of the absorption spectrum show that there is a dissociation limit for the excited electronic state of O_2 at 7.049 e.v. The ground state of oxygen is 3P , and there are low-lying 1D and 1S states with energies of 1.967 and 4.190 e.v. respectively. Thus possible products for the excited state would be $^3P + ^3P$, $^3P + ^1D$, $^3P + ^1S$, $^1D + ^1D$, $^1S + ^1S$ and $^1D + ^1S$. The rotational analysis of the spectrum shows, however, that the upper electronic state is of the type $^3\Sigma_u^-$; thus since the combination of singlet states cannot give a triplet molecular state it follows at once that the last three possibilities are ruled out. The Wigner-Witmer rules also bar the production of a $^3\Sigma_u^-$ state from $^3P + ^3P$, so that only the possibilities $^3P + ^1D$ and $^3P + ^1S$ remain. These would lead to dissociation energies for the normal oxygen molecule of 7.049 - 1.967 and 7.049 - 4.190, that is 5.082 and 2.859 e.v. respectively. The last value is absurd because the vibrational levels for the ground state are known from the analysis of the spectrum up to energies exceeding this, so that we are left with 5.082 e.v. as the only possible value for the dissociation energy of normal oxygen.

Dissociation of CO and CN ; Heat of Sublimation of Carbon.

The latent heat of sublimation of solid carbon (graphite) is a quantity which occurs frequently in thermochemical equations and one which is very difficult to determine experimentally owing to the very high temperature at which carbon sublimes. Herzberg^{122 123} has pointed out that this heat of sublimation, L , could readily be determined from the heat of dissociation of carbon monoxide, $D(CO)$, and oxygen, $D(O_2)$, and the heat of combustion of solid carbon to carbon monoxide, which is known from thermochemical measurement to be 27.40 k.cal. Thus



$$\text{giving } C_{gas} - C_{solid} = L = D(CO) - \frac{1}{2}D(O_2) - 27.40 \text{ k.cal.}$$

The heat of dissociation of O_2 is, as we have already seen, 117.2 k.cal./mol., so that $L = D(CO) - 86.0 \text{ k.cal.}$

In the spectrum of carbon monoxide, the well-known Ångström bands show predissociation which occurs in the $B^1\Sigma^+$ upper level

and gives a dissociation limit for CO at $89,620\text{ cm}^{-1}$. There is, however, some difficulty in assigning the products of the dissociation. The carbon atom could conceivably be ejected in either the 3P ground state or in a 1S , 1D or 5S excited state, while the oxygen might be in either the ground 3P or the excited 1D or 1S state. This gives a number of possibilities for the dissociation energy of CO and the heat of sublimation of carbon which are listed in Table 7; the values for $D(\text{CO})$ are given in cm^{-1} , e.v., and k.cal./mol., the latest values for the conversion factors being used; combinations of dissociation products giving $D(\text{CO})$ less than 6.5 e.v. are omitted as being obviously impossible because vibrational levels for the ground state of CO are known up to nearly this energy.

TABLE 7

Dissociation products C O		Atomic excitation cm^{-1}	$D(\text{CO})$			Latent heat of carbon k.cal.
			cm^{-1}	e.v.	k.cal.	
3P	3P	0	89,620	11.11	256.1	170.1
1D	3P	10,192	79,428	9.85	227.0	141.0
3P	1D	15,868	73,752	9.14	210.8	124.8
1S	3P	21,647	67,973	8.43	194.3	108.3
1D	1D	26,060	63,560	7.88	181.7	95.7
3P	1S	33,793	55,827	6.92	159.5	73.5
5S	3P	(34,994?)	(54,626)	(6.77)	(156.1)	(70.1)

The value of $D(\text{CO})$ obtained by Birge and Sponer¹⁸ by extrapolation of the known vibrational levels of the ground state to the dissociation limit was 11.18 e.v.,* but Herzberg gave reasons, based partly on the observation of other doubtful predissociations in the spectrum of CO, for favouring the value of 9.14 e.v., while Schmid and Gerö²¹² favoured the still lower value of 6.92 e.v. Recently, however, evidence has accumulated to show that the highest value, 11.11 e.v., is almost certainly correct. Herzberg showed that by using thermochemical data for the heat of combustion of carbon monoxide to dioxide, for the heat of combustion of cyanogen to carbon dioxide and for the heat of dissociation of C_2N_2 to 2CN , the value of $D(\text{CO})$ could be linked with $D(\text{CN})$; by spectroscopic observation of the concentration of CN in an electric discharge through C_2N_2 , White²⁴⁹ has arrived

* The author has checked this extrapolation and obtained a value of 11.2; the value for $D(\text{CO})$ could hardly be brought as low as 9.85 e.v., and certainly not as low as 9.14.

at a value of 146 k.cal. for the heat of dissociation of C_2N_2 into 2CN, from which it can be shown that $D(CN) = D(CO) - 108$ k.cal. The heat of dissociation of CN is not known with certainty, but extrapolation of the vibrational levels of the ground state gives a value of around 160 k.cal., a value which is perhaps a little high but strongly favours the highest value for $D(CO)$ given above, this leading to $D(CN) = 148$ k.cal. Penney and Kynch^{196 197} have also made estimates of the short-wave limit of the fluorescence spectrum of benzene and of the absorption spectra of polyenes which favour the 11.11 e.v. value for $D(CO)$. This is also supported by Baughan's calculations¹³ on organic bond energies which require a value of L of around 170. Marshall and Norton¹⁷² have obtained a value of 177 k.cal. for L by direct measurement. Thus all the recent evidence points to the following values,

$$D(CO) = 11.11 \text{ e.v.} = 256.1 \text{ k.cal.}$$

$$D(CN) = 6.4 \text{ e.v.} = 148 \text{ k.cal.}$$

$$L = 170.1 \text{ k.cal.}$$

Polyatomic Molecules.

It is not usually possible to determine dissociation heats of polyatomic molecules by spectroscopic methods. Combination of thermochemical data with spectroscopically determined values for the heat of dissociation of diatomic molecules, however, frequently enables the heat of formation of the polyatomic molecule to be determined.

Thus taking the heat of the reaction $CO + \frac{1}{2}O_2 = CO_2$ as 67.6 k.cal. and using the values already given for $D(O_2)$ and $D(CO)$ we obtain for the energy required to dissociate CO_2 into normal CO and O the value 126.2 k.cal., while for the complete dissociation into C+2O, that is the heat of formation of CO_2 , the energy required is 382.3 k.cal./mol.

From calculations based on their observations of the infra-red absorption spectrum of CO_2 , Adel and Dennison² have obtained a value of about 300 k.cal./mol. for the heat of dissociation of CO_2 into an oxygen atom and a carbon monoxide molecule. The difference between this value and the value 126.2 k.cal. given above should presumably correspond to the activation energy of either the oxygen atom or the carbon monoxide molecule formed by the dissociation process. The difference, of the order 174 k.cal.,

is obviously far too much for the activation energy of CO to the 1D state, but might well correspond to excitation of the CO molecule. The $a^3\Pi$ state of CO requires 48,438 cal. or 138 k.cal./mol. and other triplet states of CO , with slightly greater excitation energy, are known. This calculation, therefore, supports the view that the dissociation products of CO_2 are normal oxygen and excited carbon monoxide.

In some cases the absorption spectra of polyatomic molecules show the usual rotational fine structure of the bands merging into a continuous absorption. This may enable an upper limit for the dissociation energy to be fixed; in this way observations of the absorption spectra of NO_2 and O_3 have enabled Mecke¹⁷⁵ to give the dissociation energies as 77 and 30 k.cal./mol. respectively, and Herzberg¹²⁰ has shown in a similar manner that normal formaldehyde dissociates into $\text{HCO} + \text{H}$ with an upper limit for D of 105 k.cal./mol., while the excited state of formaldehyde has a dissociation energy of about 195 k.cal. and probably dissociates into a normal CH_2 radical and an excited oxygen atom $\text{O}(^1D)$.

Many calculations of the strength of the various types of chemical bond which occur frequently in organic molecules have been made. These mathematical calculations are partly based on spectroscopic data and are of importance in determining the activation energies required for the molecules to undergo chemical reaction. A discussion of this subject would be out of place here. It is probably sufficient to record that Baughan¹³, using nearly the same value for the heat of sublimation of carbon as that given above, has recalculated the bond strengths given by Pauling¹⁹⁴ and Sidgwick²¹⁸, and gives the following values (average):

C—H	98.5 k.cal./mol.
C—C	81.2 k.cal./mol.
$\text{C}=\text{C}$	144 k.cal./mol.

The strengths of these and similar bonds are of importance in determining the activation energy required to initiate combustion processes. The subject has, however, passed out of the hands of the spectroscopist into those of the mathematician, to whom we may look for promising developments in this important field.

The normal state of the carbon atom is 3P , but in organic

compounds carbon normally shows a valence of four. This "valence state" of carbon may therefore be considered as an excited state. It has been shown by Voge²⁴² that several of the electronic states of carbon contribute to the energy of this valence state, the 5S level of atomic carbon playing a relatively important part. This 5S level has not been determined experimentally as no spectrum line involving it has been observed, but Bacher and Goudsmit⁶ were able to calculate its position as about $34,994\text{ cm}^{-1}$ (or 4.3 e.v.) above the ground state, but Van Vleck²⁴¹ expressed the opinion that the 5S was between 5 and 8 e.v. above the ground state and gave his "valence state" as about 7 e.v. Voge's later calculations confirmed this value, but suggest that resonance might lower it by about 2.5 e.v. This energy of activation of the carbon from the 3P state to the tetravalent state will enter into all combustion processes, such as the breaking up of hydrocarbons to CH , or oxidation of CH or CO to CO_2 , in which the carbon changes from the tetravalent to the divalent form or vice versa.

CHAPTER XV

KINETIC SPECTROSCOPY

IN this concluding chapter I propose to give a few personal ideas of the lines along which the application of spectroscopy to the theory of combustion may be developed most profitably. I shall point out the need for quantitative rather than qualitative observations, and stress the use of spectroscopic data in following the details of the change—the kinetics of the combustion process.

Emission Spectra.

Most of the early studies on the emission spectra of flames were purely qualitative, and were aimed at finding out what intermediary substances were formed during the combustion. The results have, of course, been of some value and have demonstrated the presence in flames of many radicals which are physically quite stable, but which are short-lived on account of their being so reactive chemically. The knowledge that these radicals are present has been of importance in providing material for the chemist to postulate numerous chain reactions. The radicals CH and C_2 , which are among the strongest emitters in hydrocarbon flames, are not, however, made use of in the principal chain mechanisms for the combustion, and this shows clearly that some quantitative estimate of the strength of the radiation and of the number of emitting molecules is required before spectroscopic results can be used without reservation.

Measurement of the absolute intensity of any particular type of radiation is not difficult in principle, but actually surprisingly few quantitative measurements have been recorded. Kondratjew and colleagues have made measurements of the rate of emission of the characteristic radiations from flames of hydrogen and carbon monoxide and have studied the quenching effect of various diluents, and similar measurements might well be made for the various spectra associated with burning hydrocarbons. The

presence of strong bands of C_2 is often taken as an indication that the flame conditions are not far removed from those for carbon deposition, and any quantitative measurement of the strength of the C_2 bands which would link C_2 formation with coking in engines would be a considerable advance in our knowledge of this difficult problem.

Quantitative measurements on the intensity of radiation can readily be translated into total number of light quanta emitted per fuel molecule consumed, and so can give some guide to whether the light emission is due to thermal causes or is a direct result of the chemical action. It is not, however, possible to deduce the number of molecules of a particular type which are present unless the electronic transition probability is known; this can sometimes be determined by quantitative measurements of the absorption spectrum. When this can be done measurement of the amount of radiation emitted may add considerably to our knowledge of the kinetics of the reaction. Thus it has been shown (page 29) that Oldenberg and Rieke's determination of the radiative life of OH radicals combined with Kondratjew's measurements of the strength of the OH radiation from the hydrogen flame prove that although the excited OH radicals are of chemical rather than thermal origin their number is so small that, even if the Bonhoeffer-Haber mechanism is of importance in the combustion of hydrogen, chain branching by production of excited OH radicals can only be a comparatively rare event.

In some cases, measurement of relative intensities within a band system can give valuable information. The best example of this at present is again Kondratjew's work on the relative intensity of the OH bands (see page 28), from which it was proved that in the low-pressure flame such excited OH radicals as are produced are formed by the Bonhoeffer-Haber mechanism. It seems that any anomalies in the relative intensities of bands in a system, such as the separation by Vaidya of the hydrocarbon flame bands into two systems, might be worth following up.

Very little work appears to have been done on the spectra of flames in the photographic infra-red. There seems no obvious reason why the region between 7000 Å. and 10,000 Å. should not be studied with profit provided spectrographs of sufficient light gathering power are employed, and the author is at present

making some preliminary observations on flame spectra in this region.

Qualitative observations of combustion spectra will probably always have some application to specific problems as a tool for determining the type of combustion which is taking place. Thus it is easy to distinguish between the initial stages of combustion of hydrocarbons, CH and C₂ bands being prominent in the spectrum, and the final stages in which the spectrum is characteristic of the burning of carbon monoxide and hydrogen. Thus spectroscopic observation readily shows that 'knock' is associated with the method of burning of the last part of the charge, while 'afterburning' is associated with the burning of the carbon monoxide which is present in the later stages of the com

Absorption Spectra.

In the chapter on absorption spectra the need for using very high resolving power has been stressed, and it has been suggested that the ultra-violet region between 2300 Å. and 1900 Å. should not be neglected. Provided sufficiently high resolving power is used, there seems no reason why radicals like CH and the emitter of the hydrocarbon flame bands should not be observed and measured quantitatively by their absorption spectrum in the same way that OH and CN have been estimated by Oldenberg and Rieke and by White respectively.

Some measurements on the infra-red absorption spectra of flames have, of course, been made, but careful quantitative measurements, and especially comparison with the absorption by hot gases of similar chemical composition, might enable an estimate to be made of the time lag in the equipartition of the vibrational energy of the newly formed CO₂ and H₂O molecules. There seems to be a very real difference between live flame products and mere hot gases, and measurements of the infra-red absorption spectrum might give some information about the nature of this difference.

The Equipartition of Energy.

Considerable space has already been devoted to a discussion of the time lag before molecules with excess vibrational energy reach thermal equilibrium with the remainder of the system.

The evidence for this time lag has been obtained from both spectroscopic observations and from measurements of supersonic dispersion. It is obviously of great importance in determining such things as the maximum temperature attained during explosions, the amount of dissociation of the gases, the amount of infra-red radiation from flames, and the effect of diluents on flame speeds, etc. It has been shown that the catalytic action of water in promoting the combustion of carbon monoxide is due to the readiness with which the water molecules convert the vibrational energy of the newly formed CO_2 molecules into thermal energy, and so raise the temperature of the flame, thus promoting the combustion and at the same time reducing the abnormal dissociation of the CO_2 molecules. Further developments along these lines may be looked for in the future.

The action of catalysts, both promoters such as ethyl nitrate and amyl nitrite, and inhibitors such as various halogen compounds (e.g. propyl bromide, iso-amyl bromide, amyl iodide), in increasing and reducing flame speeds is little understood. Recently West and Miller ²⁴⁵ in studying the fluorescence of certain hydrocarbons in solution have found evidence for a resonance transfer of energy from the photo-activated hydrocarbons to various alkyl iodides. This suggests that the action of alkyl halides as inhibitors may be due to their deactivating energy-rich hydrocarbon compounds engaged in propagating the combustion process. Experiments on the quenching of fluorescence in the gas phase might well be carried out as a first check on this hypothesis.

Homomolecular molecules such as O_2 , H_2 and N_2 are of course inactive as far as infra-red radiation is concerned. Thus it follows that if these molecules acquire vibrational energy this energy cannot be lost by radiation, but only on collision. There is evidence, from supersonic measurements, that the vibrational energy is not quickly converted into other forms by collision, so that there will be a considerable amount of transference of this vibrational energy from one molecule to another before the energy is degraded to other forms. These molecules might therefore serve a purpose in propagating energy chains during the combustion processes.

Peroxidation *versus* Hydroxylation.

The controversy between the rival peroxidation and hydroxylation theories of hydrocarbon combustion has already been mentioned in Chapter IV. Spectroscopic studies have not so far decided conclusively between the two theories, but some evidence has been put forward in favour of the peroxide theory. Guénault has pointed out that the flame of methyl alcohol shows the bands usually associated with the cool flame of ether, while the flame of methane does not, indicating that methyl alcohol is not an intermediary in the combustion of methane. My own experiments on chilled flames have clearly demonstrated that the hydrocarbon (or ethylene) flame bands, which occur in the inner cone of hydrocarbon flames, are associated with the formation of alkyl peroxides. Any further evidence on the nature of the emitter of these hydrocarbon flame bands and any quantitative work which would give a measure of their relative importance in the combustion process would be of great value.

The spectra of flames supported by atomic oxygen are in all ways very similar to normal flame spectra. This would at first sight appear to be evidence that atomic oxygen might play a part in normal flames (Norrish's modified hydroxylation theory), but this is more than discounted by the fact that methane will not give a flame with atomic oxygen. It is a great pity that spectroscopic methods are unsuitable as a test for the presence of atomic oxygen. The absorption lines of oxygen lie far down in the vacuum ultra-violet and there seems little prospect of using them for testing for the presence of oxygen atoms in combustion. The high dissociation energy of oxygen makes it seem unlikely that the amount of dissociation at flame temperatures would be sufficient to produce enough atoms to maintain the reaction chains. Some form of peroxide theory would therefore seem to fit the facts rather better.

The Details of Combustion Processes.

Chemists interested in combustion processes have naturally aimed largely at expressing the various chemical reactions, and especially the chain mechanisms by which the combustion is maintained, by ordinary chemical equations, supplemented in some cases by thermochemical data. Physicists, and more

especially spectroscopists, are, however, interested in many of the finer details of the chemical reactions and collision processes.

For any process, such as, for example, the combustion of methane, it is usually possible to write down a large number of conceivable chemical equations to describe the initiation and maintenance of the reaction. By taking into account the ordinary kinetics of the reaction, such as its dependence on pressure and concentration of the various reactants, and by using any thermochemical data which may be available, the number of practically possible ways in which the reaction can proceed can be reduced, so that the process may be represented by one or more series of chemical equations. These do not, however, give a complete picture of the reaction. We may ask whether an activation energy is required, and whether this activation energy must take any special form such as translational energy of approach of the reactants, internal vibrational energy, or energy of electronic excitation of one of the reactants; whether the products are normal or electronically excited molecules; in what form the energy of the reaction is liberated; what is the after history of this energy, i.e. whether it is dissipated as thermal energy, radiated, or retained to propagate the combustion process; whether any collision complexes are formed and what is their mean life.

It is seldom possible to give a precise answer to most of these questions, but considerable progress has been made in the last ten years and still more may be expected in the future. Studies of molecular structure and stability, and of the strength and interaction between various types of chemical bond owe much to the development of the theory of molecular spectra, and in actual calculations values of the various vibrational frequencies of the molecules as determined from observations of their infrared and Raman spectra are used. This subject is of general interest to chemistry, but molecular stability and the method of decomposition of various molecules are of particular interest to the theory of combustion.

Many chemical reactions are believed to be propagated by energy chains. Before postulating an energy chain due consideration should, where possible, be given to the form such energy will take. Some molecules such as acetylene and formaldehyde show discrete absorption bands and therefore possess physically stable excited electronic states and may therefore

retain any activation energy in the form of electronic excitation. Other molecules such as H_2O , and most organic acids and peroxides only show continuous absorption spectra; this means that their excited electronic states are repulsive, so that these molecules cannot retain electronic activation energy, but would decompose in a time short compared with that between collisions. These molecules could, of course, retain some energy in the form of internal vibration, but the amount of this must be limited, and in cases where the bond strengths are small, as in organic peroxides, only a very little energy can be carried without the molecule decomposing spontaneously.

In future applications of spectroscopy to combustion problems we may look for a more dynamic approach to the subject. A brief section has been devoted to the spectroscopic evidence for the formation of collision complexes and to the mathematical determination of the life of these activated complexes. The details of the collision processes and especially the effect of the electronic configurations of the colliding molecules on the probability of reaction occurring and the type of product formed are likely to become of increasing interest. We have seen that if normal carbon monoxide and normal oxygen combine the resulting carbon dioxide molecules will initially be formed in an excited electronic state, and that the loss of this electronic energy still leaves the molecules with an excess of vibrational energy which greatly influences the combustion processes. For all saturated hydrocarbons, and indeed organic compounds generally, the carbon is in the tetravalent state, while in CO , and probably in CH , C_2 and certain radicals, it is divalent; thus during the combustion of hydrocarbons the carbon atoms may undergo several changes in valency before the final product, carbon dioxide, is formed, and so we may expect some complications in the details of the combustion mechanism. Developments in this field must await more fundamental work on the electronic structure of polyatomic molecules and the interaction between various types of electronic configuration. In the last few years Mulliken has published a long series of papers (in *Phys. Rev.* and *J. Chem. Phys.*) on the electronic structure of various classes of polyatomic molecule, and it may be hoped that these results will ultimately be used to furnish details of the kinetics of combustion processes.

DESCRIPTION OF PLATES

ALL the reproductions are enlargements of spectrograms taken on a medium size (Hilger E.2) quartz instrument, except Plates 1e and 2a, which were taken on a small quartz spectrograph.

PLATE 1. (To face page 34.)

- (a) Hydrogen flame burning at silica jet in air. Zenith plate (non colour sensitive). The plate shows a little scattered sunlight (solar spectrum) as well.
- (b) Carbon monoxide-air flame. Half-tone plate (high contrast, non colour sensitive).
- (c) Outer cone of ethylene-air flame. Zenith plate. Wide slit.
- (d) Inner cone of ordinary Bunsen flame. Panchromatic plate.
- (e) Chilled flame of town's gas (see page 34). Fast Blue Sensitive plate (not sensitive to green or red regions).

PLATE 2. (To face page 70.)

- (a) Cool (phosphorescent) flame of ether. Copper arc comparison. Wide slit. I am indebted to Dr. H. J. Emeléus for the loan of the negative of this spectrum.
- (b) Inner cone of Bunsen flame with ethyl nitrate introduced into the gas supply. Zenith plate.
- (c) Oxy-ammonia flame, reproduced from Fowler and Badami ⁷⁴ with the aid of a cylindrical lens.
- (d) Inner cone of an acetylene-air flame. Heavy exposure on a half-tone plate to show predissociation in the weaker CH bands.
- (e) Absorption spectrum (using hydrogen discharge as source of continuum) taken during the slow combustion of a mixture of pentane and oxygen. This plate shows formaldehyde bands and some continuous absorption towards the far ultra-violet. I am indebted to Professor A. C. Egerton and Dr. G. H. Young for the use of the negative of this plate.

APPENDIX

I. BAND SYSTEMS EMITTED BY ORGANIC FLAMES

IN the following tables the wave-lengths (λ) in international angstroms, the intensities (I) on a scale of 0 to 10 based on uncorrected visual estimates, and the assignment of vibrational quantum numbers (v' , v'') are given for those band systems which normally occur in the flame spectra of organic compounds containing oxygen, hydrogen and nitrogen. Outstanding band heads are denoted by the letter S (sequence) following the intensity. Some other band systems frequently encountered in flame spectra are given in the second section of this appendix, and band systems which are or may be observed in absorption during combustion processes are listed in a similar way in the third section. For details of other band systems in the visible and quartz ultra-violet region, the reader is referred to the book on *The Identification of Molecular Spectra* by Pearse and the author¹⁹⁵, in which are given similar details for all known diatomic band spectra and many systems due to polyatomic molecules.

C₂ Swan System.

These bands, which are due to a ${}^3\Pi \rightarrow {}^3\Pi$ transition, have single heads and form marked sequences. They are degraded to the violet. Measurements from Jevons¹³⁴. See Plate 1d.

λ	I	v', v''	λ	I	v', v''	λ	I	v', v''
6677.3	1	2, 5	5958.7	2	4, 6	5097.7	1	2, 2
6599.2	1	3, 6	5923.4	1	5, 7	4737.1	9S	1, 0
6533.7	2	4, 7	5635.5	8S	0, 1	4715.2	8	2, 1
6480.5	2	5, 8	5585.5	8	1, 2	4697.6	7	3, 2
6442.3	2	6, 9	5540.7	6	2, 3	4684.8	4	4, 3
6191.2	3S	0, 2	5501.9	4	3, 4	4678.6	2	5, 4
6122.1	4	1, 3	5470.3	2	4, 5	4382.5	2S	2, 0
6059.7	3	2, 4	5165.2	10S	0, 0	4371.4	4	3, 1
6004.9	3	3, 5	5129.3	6	1, 1	4365.2	5	4, 2

CH.

4315 A. System.

The bands are due to a ${}^2\Delta \rightarrow {}^2\Pi$ transition and are degraded to the violet. They show fairly open rotational fine structure. Measure-

ments from Raffety ²⁰³, Grenat ¹⁰⁴, and Geib and Vaidya ⁹⁵. See Plate 1*d*.

λ	I	v', v''
4942	1S	0, 1
4937.5	1	
4890.0	1	
4384	3	0, 0
4315.0	3	
4312.5	10S	

3900 A. System.

These bands are due to a $^2\Sigma \rightarrow ^2\Pi$ transition, and are degraded to the red. The rotational fine structure is very open. Measurements by Raffety ²⁰³ and Grenat ¹⁰⁴. See Plates 1*d* and 2*d*.

λ	I	v', v''
3628	1S	1, 0
3872	5S	0, 0
3889.0	4	
4025.3	1	1, 1

3143 A. System.

This band is due to a $^2\Sigma \rightarrow ^2\Pi$ transition. The band is not degraded strongly and appears usually with a maximum of intensity at 3143 A., the appearance being rather like that of a broad atomic line.

CN Violet System.

These bands, which are due to a $^2\Sigma \rightarrow ^2\Sigma$ transition, have single heads and form marked sequences. They are degraded to the violet. Measurements from Jevons ¹³². See Plate 2*b*.

λ	I	v', v''	λ	I	v', v''
4216.0	4S	0, 1	3871.4	9	1, 1
4197.2	5	1, 2	3861.9	8*	2, 2
4181.0	5	2, 3	3854.7	7	3, 3
4167.8	4	3, 4	3851	6	4, 4
4158.1	4	4, 5	3590.4	6S	1, 0
4152.4	4	5, 6	3585.9	6	2, 1
3883.4	10S	0, 0	3583.9	6	3, 2

* The (0, 0) and (1, 1) bands are often masked by the CH bands in flame spectra. In this case the (2, 2) band is outstanding at the head of a group of three bands. See Plate 2*d*.

NH.

3360 Å. System.

These bands are due to a ${}^3\Pi \rightarrow {}^3\Sigma$ transition, and are not clearly degraded in either direction. The usual appearance of the bands is of a strong, almost line-like, maximum of intensity at 3360 Å. (the piled up Q branch of the 0, 0 band) and a rather less strong maximum of similar appearance at 3370 Å. (the 1, 1 band) with regularly spaced open rotational fine structure stretching out for some distance on either side of these line-like maxima. See Plates 2b, 2c.

λ	I	v', v''
3360	10	0, 0
3370	5	1, 1

3240 Å. System.

This system does not usually appear readily in flames, but has been observed in chemiluminescence by Gleu⁹⁹. The (0, 0) band has heads at 3240.1 and 3253.4 Å., and the band is shaded to the red.

NO, γ System.

These bands are due to a ${}^2\Sigma \rightarrow {}^2\Pi$ transition, and are double-double headed. The strong bands form a single $v' = 0$ progression. The rotational structure is less open than that for hydride molecules, but is often visible with medium-size quartz spectrographs. Measurements compiled from Bair⁹, Guillery¹⁰⁷, Schmid²¹⁰ and Strutt²²³. The P_1 (first) and P_2 (third) heads are given. The bands are degraded to shorter wave-lengths. See Plate 2c.

λ	I	v', v''	λ	I	v', v''	λ	I	v', v''
3008.8	4S	0, 6	2680.0	5	1, 5	2478.7	10S	0, 2
2997.6	4		2671			2471.1	10	
2859.5	6S	0, 5	2595.7	10S	0, 3	2370.2	9S	0, 1
2849.8	6		2587.5	10		2363.3	9	
2722.2	9S	0, 4	2558.6	5	1, 4	2269.4	5S	0, 0
2713.2	9		2551	5		2263.0		

OH.

The bands are due to a ${}^2\Sigma \rightarrow {}^2\Pi$ transition and have four heads each, the first, second and fourth being more definite than the third head, which is seldom seen clearly. The bands are degraded to the red, and show open rotational fine structure. See Plate 1a. In the following table the prominent heads only are given, the type of branch forming the head being indicated. Measurements are compiled from Watson²⁴⁴, Grebe and Holtz¹⁰³ and Jack^{129 130}.

λ	I	v', v''	λ	I	v', v''
2608.5	2S	2, 0 R ₂	2945.2	3	3, 1 R ₂
2613.4	2	R ₁			
2622.1	2	Q ₁	3063.6	10S	0, 0 R ₂
			3067.2	10	R ₁
2677.3	2	3, 1 R ₂	3078	5	Q ₂
2683.1	2	R ₁	3089	10	Q ₁
2691.1	2	Q ₁			
			3121.7	—	1, 1 R ₂
2811.3	4S	1, 0 R ₂			
2816.0	3	R ₁	3428.1	2S	0, 1 R ₂
2829.0	4	Q ₁	3432.1	2	R ₁
			3458.5	2	Q ₂
2875.3	3	2, 1 R ₂	3472.1	3	Q ₁
2892.7	3	Q ₁			

The Carbon Monoxide Flame Bands (CO₂).

The carbon monoxide flame shows a strong continuous spectrum stretching from below 3000 Å. to beyond 5000 Å., a large number of narrow headless bands being superposed on this continuum. The spectrum is best identified by comparison of photographs. The following are the approximate positions of the strongest bands, compiled from Weston ²⁴⁶, Kondratjew ¹⁴⁵ and the author ⁸⁹. Many of the longer wave-length bands, when examined with fair dispersion and plates of high contrast are found to be double. See Plate 1b.

λ	λ	λ	λ	λ
5430	4980	4674	4411	4104
5318	4933	4646	4344	4093
5276	4893	4567	4335	4045
5169	4798	4553	4260	4035
5129	4768	4527	4156	3912

The Hydrocarbon (or Ethylene) Flame Bands (HCO ?).

These bands are degraded to the red. See Plate 1c. The following measurements of the strong bands are by Vaidya ²³⁶, who arranged the system into two groups.

Group A.

λ	I	λ	I	λ	I
2585.5	3	2858.0	6	3502.7	8
2618.0	3	2948.2	7	3588.6	8
2658.8	4	3014.8	8	3635.6	3
2716.0	5	3299.2	10	3730.5	5
2751.5	4	3377.4	10	3824.9	4
2797.1	5	3417.4	3	4092.0	3

Group B.

λ	I	λ	I
2704.5	1	3472.5	5
2780.4	2	3569.2	3
3001.5	2	3697.7	4
3359.0	5	3802.7	2

The Cool Flame Spectrum of Ether (Formaldehyde Fluorescence, HCHO).

This system consists of a number of narrow bands probably degraded to the red. Identification is best by comparison of spectrograms. See Plate 2a. The formaldehyde has been studied by Herzberg and Franzen¹⁰², while the cool flame has been photographed by Emel us⁶¹. The following measurements, mostly by He Franz, are taken from Kondratjew¹⁴⁷, using Emel us's in

λ	I	λ	I	λ	I
(3410)	2	3959.6	9	4447.6	7
(3540)	4	4053.3	5	4566.8	7
3706.3	8	4129.2	8	4707.1	5
3767	3	4242.8	8	4821	3
3855.5	8	4359.9	7	4942	1

II. OTHER BAND SYSTEMS WHICH OCCUR FREQUENTLY IN FLAMES

IN these tables are listed those band systems which occur readily in flames, either as a result of the combustion itself or as impurities. The systems are given in alphabetical order of the chemical symbols of the emitting molecules ; the ethyl bromide flame bands, the methyl iodide flame bands, and the ammonia α bands are listed under BrO, IO and NH_2 respectively. See also note at the beginning of Appendix I.

Br₂.

These bands occur in the outer cones of flames containing bromine, the flame being coloured orange-red. The system consists of a very large number of bands, which are degraded to the red, although this fact is not obvious in most spectrograms of flame spectra showing them. The system has been studied by Kuhn ¹⁵⁸, Brown ³², Darbyshire ⁴⁰, Uchida ²³³, Kitagawa ¹⁴³ and Vaidya ²³⁹, and the following list of the strongest bands has been compiled by averaging the wavelengths given in the above references.

$\lambda\lambda$ 6546, 6472, 6415, 6364, 6342, 6312, 6291, 6263, 6239, 6220,
6189, 6168, 6120, 6071, 5957, 5942, 5864, 5826, 5752, 5725,
5603, 5588.

BrO ? Ethyl Bromide Flame Bands.

The bands are degraded to the red and appear to be due to a diatomic emitter. Vaidya ²³⁹, whose measurements are given here, attributed the bands provisionally to BrO, but CBr also seems a possibility.

λ	I	v', v''	λ	I	v', v''
4029.2	3	0, 0	4269.8	7	0, 2
4065.8	4	—	4399.4	7	0, 3
4147.0	5	0, 1	4430.2	4	3, 4
4178.1	5	1, 2	4534.2	8	0, 4

CCl.

Observed by Vaidya ²⁴⁰ in the flames of CH₂Cl, CHCl₃, and CCl₄. Each band has about four heads, degraded to shorter wave-lengths. Measurements by Asundi and Karim ³.

λ	I	λ	I	λ	I
2862.0	0	2795.9	6S	2778.8	6
2856.8	4	2789.8	8	2777.6	8
2849.4	4	2788.3	8	2724.3	0
2845.8	4	2786.6	5	2713.4	0
		2782.3	8		

CS.

The bands are probably due to a ${}^1\Pi \rightarrow {}^1\Sigma$ transition, and have close double heads. They are degraded to the red and form fairly well marked sequences. The following measurements of the wave-lengths are by Jevons ¹³³.

λ	I	v', v''	λ	I	v', v''
2507.3	3S	1, 0	2605.9	5	2, 2
2523.2	4	2, 1	2621.6	3	3, 3
2538.7	4	3, 2	2662.6	5S	0, 1
2575.6	10S	0, 0	2677.0	4	1, 2
2589.6	7	1, 1	2693.2	3	2, 3

CaO.

These bands have been observed as impurities both in flames and in explosions. Seen with small dispersion, the bands appear to be diffuse and shaded to the violet.

λ	I
6500	4
6260	10
6035	3
5560	6

Under larger dispersion the bands may be seen to be much more complex, with heads degraded in both directions. A reproduction of a spectrogram, using an arc source, and tables of wave-lengths are given by Pearse and the author ¹⁹⁵.

FeO.

These bands occur when iron carbonyl is introduced into a flame, and also frequently as an impurity. Most of the bands are degraded

to the red, but in some cases narrow headless structures are observed. Measurements of the strongest bands by the author ¹⁹⁵.

λ	I	λ	I	λ	I	λ	I
5531.4	4	5624.1	4	5903.0	6	6109.9	9*
5545	2	5646.6	6	5911	4*	6180.5	9S
5582.8	6S	5789.8	9S	5919	4*	6218.9	10
5614.0	6	5819.2	6	5974.6	6	6524.1	2S
5621.3	4	5868.1	9	6097.3	9*	6566.7	2

* Maximum of intensity of narrow headless structure.

IO ? Methyl Iodide Flame Bands.

This system was observed by Vaidya ²³⁸ in the flame of methyl iodide mixed with methyl alcohol or coal-gas, the bands being emitted most strongly in the green region of the flame just above the inner cone. Vaidya attributed the bands provisionally to IO, but CI also seems a possibility. The bands are degraded to the red and form two systems.

System A.

λ	I	v', v''	λ	I	v', v''	λ	I	v', v''
4267.8	4	3, 0	4485.0	7	1, 1	4686.2	8	1, 3
4353.7	5	—	4549.2	5	0, 1	4725.6	6	2, 4
4384.3	4	1, 0	4583.0	10	1, 2	4757.8	4	3, 5
4445.9	5	0, 0	4621.1	6	2, 3	4780.5	4	4, 6

System B.

λ	I	v', v''
4838.5	8	1, 0
4960.4	4	0, 0
5125.9	6	0, 1
5301.8	6	0, 2
5488.9	5	0, 3
5522.6	4	1, 4
5686.0	4	0, 4

NH₃, Ammonia α Band.

This band occurs in the oxy-ammonia flame, being responsible for its yellow-green colour. The band, which is strongest in the yellow and green region, is composed of a very large number of fine lines due to the rotational structure, and does not show any heads or obvious regularity. Measurements of some 300 lines are given by Rimmer ²⁰⁷ and some of the strongest lines are quoted by Pearse and the author ¹⁹⁵.

According to Fowler and Badami ⁷⁴ the band shows apparent heads, under small dispersion, at $\lambda\lambda$ 6652*, 6470, 6302*, 6042*, 5870, 5713*, 5575, 5436*, 5384 and 5265, the brighter bands being marked by an asterisk. See Plate 2*d*.

NiH.

Bands with very open rotational structure, observed when nickel carbonyl is introduced into a flame. The bands are due to $^2\Delta \rightarrow ^2\Delta$ transitions, and form two heads each. They are degraded to the red. Measurements by Gaydon and Pearse ⁹⁴.

System A.

λ	I	v', v''
6425.1	4	0, 0

System B.

λ	I	v', v''
5290.0	2	2, 0
5712.5	6	1, 0
6246.0	10	0, 0

PO. *β System.*

There is a strong sequence of bands commencing at around 3240 Å. and getting weaker to longer wave-lengths. This sequence has no marked head, and the bands of which it is formed show heads degraded in both directions. There are two similar weaker sequences further to the red. The bands are due to a $^2II \rightarrow ^2II$ transition, and have been studied by Geuter ⁹⁷, Petrikaln ¹⁹⁸ and by Curry, Herzberg and Herzberg ⁹⁹. The following measurements of wave-lengths and intensities (on a scale of 6) are for an arc source. The letters R and V are used to indicate whether the head is degraded to the red or violet.

λ	I	λ	I	λ	I	λ	I
3424.7 V? 3		3379.8 V 3		3285.8 R 3		3266.7 V? 3	
3414.2 V 3		3346.3 R 3		3280.7 V? 4		3255.3 V 6	
3405.8 V 3		3328.4 R 4		3270.5 V 6		3253.4 R 5	
3397.9 V 3		3311.9 R 5		3268.9 R 5		3246.3 V 6	
3388.0 V 3		3296.4 R 5					

 γ System.

These bands are due to a $^2\Sigma \rightarrow ^2II$ transition and show double-double heads. The bands are degraded to shorter wave-lengths, and the sequences are fairly well marked. The following are the P_1 and P_2 heads of the strongest bands as measured by Ghosh and Ball ⁹⁸.

λ	I	v', v''	λ	I	v', v''
2636.3	7S	0, 2 P_1	2477.9	10S	0, 0 P_1
2620.5	8	0, 2 P_2	2464.2	10	0, 0 P_2
2555.0	10S	0, 1 P_1	2396.3	7S	1, 0 P_1
2540.4	10	0, 1 P_2	2383.5	7	1, 0 P_2

PbO.

These bands are observed in flames containing lead tetraethyl. All the bands, which have been arranged into several systems, are single headed and are degraded to the red. They have been studied by Bloomenthal ¹⁹, Howell ¹²⁵ and Withrow and Rassweiler ²⁵².

λ	I	λ	I	λ	I	λ	I
3209.2	6	4229.0	10	4816.9	8	5910.7	8
3264.4	6	4317.1	10	4983.8	5	6160.5	8
3401.9	10	4410.4	8	5138.2	5	6250.7	9
3485.7	10	4553.7	10	5459.4	7	6427.7	7
4146	8	4658.0	10	5677.8	9	6475.8	7

S₂.

This is a very extensive system consisting of a large number of bands which are degraded to the red. The system extends from 2769 Å. to the near infra-red, but in flame sources the bands with low values of v' appear most strongly, and the appearance is less complex. The following measurements are based on those by Fowler and Vaidya ⁷⁸.

λ	I	v', v''	λ	I	v', v''	λ	I	v', v''
3369.4	4	2, 4	3587.2	7	1, 6	4045.6	10	0, 10
3416.8	5	1, 4	3645.0	8	0, 6	4157.0	8	0, 11
3469.4	4	0, 4	3739.8	10	0, 7	4193.6	8	1, 12
3500.3	6	1, 5	3837.1	10	0, 8	4310.8	8	1, 13
3555.6	4	0, 5	3938.9	10	0, 9	4433.4	8	1, 14

SO.

Single-headed bands degraded to the red. Measurements by Henri and Wolff ¹¹⁹ and by Martin ¹⁷³.

λ	I	v', v''	λ	I	v', v''
2664.8	5	1, 2	3164.8	10	0, 7
2744.0	6	1, 3	3271.0	10	0, 8
2827.4	8	1, 4	3383.1	6	0, 9
2968.5	5	0, 5	3548.7	6	1, 11
3064.1	10	0, 6	3676.2	7	1, 12

SiO.

A system of single-headed bands degraded to the red. Measurements by Jevons ¹³¹.

λ	I	v', v''	λ	I	v', v''	λ	I	v', v''
2344.3	4S	0, 0	2481.9	3	3, 4	2644.8	4	0, 4
2365	4	1, 1	2486.8	10S	0, 2	2669.0	8	1, 5
2387.9	3	2, 2	2509.9	3	1, 3	2693.7	7	2, 6
2413.8	7S	0, 1	2563.8	8S	0, 3	2755.0	6	1, 6
2459.0	3	2, 3	2587.1	8	1, 4	2780.5	6	2, 7

III. ABSORPTION SPECTRA

IN the following tables are listed briefly some of the absorption spectra of frequent interest in combustion work. Some band systems, such as those of benzene and sulphur dioxide, which often occur as impurities, are also included. See also note at the beginning of Appendix I.

C_6H_6 , Benzene.

The absorption by benzene is very strong and frequently appears as an impurity. Coal-gas shows benzene absorption slightly. The bands form well-marked sequences which are degraded to the red, the following measurements of the heads of these sequences, with intensities in parentheses, being by Henri ¹¹⁶.

2363.5 (3), 2415.9 (5), 2471.0 (9), 2528.6 (10), 2589.0 (9), 2667.1 (1).

CH_2O , Formaldehyde.

This band system has frequently been observed in the absorption spectra of hydrocarbons, etc., undergoing slow combustion. See Plate 2e. Under moderate dispersion the bands, of which there are a fairly large number often occurring in pairs, appear to be degraded to the red, but with larger dispersion this degradation of the bands is less obvious because of the complexity of the rotational fine structure. The bands have been studied in detail by Henri and Schou ¹¹⁸. The following are the approximate positions of the stronger band heads as seen under moderate dispersion,

λ	I	λ	I	λ	I	λ	I
2706?	3	2874?	6	3033?	9S	3164	9
2747	5	2931	10S	3051	7	3250?	7S
2787	6	2948	6	3085?	5	3288	6
2839	9S	2979	6	3135?	8S	3387	4S

CH_3CHO , Acetaldehyde.

These bands are less sharp in appearance than those of formaldehyde, and in the following table the limits of the rather broad bands, as measured by Schou ²¹³, are given. Some of the bands appear to be shaded to the red. Beyond 3200 A. the bands become

more diffuse, and merge into a continuum beyond 2800 Å. The absorption is strongest around 2900 Å.

$\lambda\lambda$	I	$\lambda\lambda$	I	$\lambda\lambda$	I
3381.1-3399.3	3	3289.9-3296.2	6	3216.9-3222.1	5
3363.0-3376.6	2	3274.4-3281.3	5	3212.7-3215.6	6
3344.5-3359.0	4	3258.3-3267.6	7	3202.0-3207.3	6
3328.9-3341.7	3	3247.3-3254.4	6	3196.1-3199.0	7
3314.7-3320.0	6	3234.1-3241.1	6	3180.2-3190.9	9
3299.9-3305.1	4	3228.7-3231.4	5	3172.2-3177.5	8

C_2H_5CHO , Propaldehyde.

Diffuse bands between 3400 Å. and 3250 Å. merging into a continuum on the short wave-length side. The following measurements of the limits of the bands are by Schou ²¹⁴.

$\lambda\lambda$	I	$\lambda\lambda$	I
3363.9-3370.8	4	3294.2-3298.1	9
3339.6-3343.6	5	3284.8-3288.7	8
3332.3-3336.1	6	3272.3-3276.7	8
3324.9-3331.4	6	3262.0-3269.0	7
3316.4-3322.0	8	3248.9-3253.7	8

C_3H_6O , Acetone.

Bowen and Thompson ³¹ have observed that the continuous absorption between 3200 and 2400 Å. observed at atmospheric pressure breaks up at low pressure into four groups each of about 25 diffuse bands; these groups have maxima at 3150, 2900, 2710 and 2570 Å.

C_6H_5CHO , Benzaldehyde.

The following estimates of the wave-lengths and intensities, in parentheses, of the narrow headless absorption bands are based on Hemptinne's ¹¹⁵ published spectrogram.

$\lambda\lambda$ 2851 (2), 2841 (10), 2806 (4), 2777 (4), 2766 (8), 2746 (6), 2735 (6), 2726 (2), 2716 (2), 2709 (4), 2696 (4), 2677 (4).

C_3O_2 , Carbon Suboxide.

The spectrum consists of a number of narrow headless bands, the following maxima of which are taken from Thompson and Healey ²²⁷.

$\lambda\lambda$ 3350, 3332, 3316, 3302, 3292, 3277, 3251, 3175, 3166, 3136, 3127, 3092, 3082, 3047, 3038, 3015, 3006, 2994, 2987, 2955, 2946.
--

HNO₂ ?

These bands have been observed by Newitt and Outridge ¹⁸⁶ in absorption in flames and explosions of carbon monoxide mixed with nitric and nitrous oxides, and the bands have also been observed in absorption by a moist mixture of nitrous and nitric oxides (Melvin and Wulf ¹⁷⁷). The bands have been attributed to NO₂ or the carrier — NO₂ (Thompson ²²⁶) as well as to HNO₂. The following measurements, with intensities on a scale of 0 to 3 given in parentheses, are by Newitt and Outridge.

λ 3845 (1),	3800 (0),	3764 (1),	3726 (2),	3680 (3),	3656 (1),
3615 (0),	3575 (0),	3545 (3),	3513 (1),	3485 (1),	3440 (0),
3418 (3),	3390 (1),	3330 (0),	3305 (0),	3270 (1),	3202 (0),
3183 (0).					

NO, Nitric Oxide.

Although nitric oxide shows two strong band systems in emission in the near ultra-violet which involve the ground electronic state, absorption bands of moderate intensity are only observed in the far ultra-violet below 2300 Å. and really strong absorption bands only occur below 1900 Å. The absorption has been studied by Liefson ¹⁶⁷ and Naudé ¹⁸⁴. The bands of the γ system given below require an equivalent thickness of more than 1 mm. of gas at atmospheric pressure for their satisfactory observation. The β bands require a very much greater thickness of gas. The γ bands are degraded to shorter wavelengths, and are double-double headed. The following are the outstanding (P₁) heads.

λ	I	v', v''
2269.4	10	0, 0
2154.9	9	1, 0
2052.4	8	2, 0

The separation between the P₁ and P₂ heads is about 6 Å., and the Q heads lie rather over 1 Å. to shorter wave-lengths of the P heads.

NO₂, Nitrogen Peroxide.

The banded absorption spectrum of nitrogen peroxide may be considered as divided into two systems, in the visible and ultra-violet regions.

The Visible System.

With small amounts of gas a number of bands are obtained in the violet region; these show sharp rotational structure, but the heads of the bands are not definite; the bands merge into a continuum towards the near ultra-violet. As the quantity of gas is increased

the absorption spreads step by step to the red, and sharp bands may be followed as far as 9000 Å. The following are some of the outstanding maxima (M) and heads degraded to the red (R) of this very complicated system. The measurements are based on those by Henri ¹¹⁷ and Harris and Pearse (see ¹⁸⁵).

λ	I	λ	I	λ	I	λ	I
5095 M	3	4795 M	3	4545 R	4	4304 R	5
5048 M	3	4740 R	5	4480 M	10	4270 R	5
5027 M	3	4630 R	6	4448 R	8	4133 M	5
4945 M	3	4605 M	3	4390 R	8	4102 M	4
4880 R	3	4580 M	4	4350 M	6	4081 R	3

The Ultra-Violet System.

The longer wave-length bands are sharp and show very open rotational structure. The bands are degraded to the red, but the shorter wave-length bands are diffuse. The absorption increases in strength towards the far ultra-violet.

λ	I	λ	I
2491.4	6 sharp	2390	8 diffuse
2459.3	5 sharp	2372	8 very wide
2446.7	5 diffuse	2363	4 diffuse, headless
2430	2 diffuse	2351	9 diffuse, headless
2419	10 diffuse		

O_2 .

The absorption by atmospheric oxygen sets the ultra-violet limit to spectroscopic work in air. At this limit bands, degraded to the red, are observed. The following measurements are by Liefson ¹⁶⁷

λ	1924.8,	1903.1,	1883.0,	1864.0,	1846.9,	1831.1,	1816.8,	1804.3,
	1793.4,	1783.9,	1775.9,	1769.2,	1763.8,	1759.6,	1755.7.	

With heated oxygen the absorption extends to longer wave-lengths and can be followed as far as 2500 Å., but in this region only complicated rotational structure is observed without definite heads. This absorption by the heated gas has been studied by Füchtbauer and Holm ⁷⁹.

SO_2 .

The strong absorption bands of sulphur dioxide are of frequent occurrence as an impurity, and also occur superposed on the emission spectra of most flames containing sulphur. The following wave-lengths of the maxima, and intensity estimates for the strongest bands are based on work by Clements ³⁸. The bands are degraded to the

red, the heads being about 1 A. to the violet of the measurements for the maxima given here.

λ	I	λ	I	λ	I	λ	I
2646.6	3	2789.4	7	2923.1	8	3087.7	4
2685.0	4	2797.0	8	2924.8	8	3108.4	3
2727.5	3	2815.5	7	2937.7	8	3129.5	?
2734.6	5	2818.1	7	2943.8	9	3131.3	3
2738.1	4	2832.3	8	2961.2	10	3151.8	2
2751.2	4	2852.0	9	2980.0	9	3159.0	2
2754.6	4	2868.9	8	3001.0	10	3167.0	1
2765.2	4	2887.7	9	3022.1	9	3173.0	1
2772.0	4	2900.9	5	3043.3	7	3181.1	1
2780.0	6	2906.5	8	3065.9	5	3190.9	1

Organic Compounds.

All the lower *paraffins* and saturated *alcohols* are transparent throughout the visible and quartz ultra-violet.

Most organic *acids* and *peroxides* show continuous absorption at the ultra-violet end of the spectrum, the strength of the absorption increasing to shorter wave-lengths.

Most *aldehydes* show diffuse bands around 3200–3000 A.

Ketones show a region of continuous absorption around 2800 A.

Most simple *benzene derivatives* show a banded absorption spectrum in the region 2600–2400 A.

Brief details of the absorption spectra of the following compounds are given by Egerton and Pidgeon⁵⁴ or Ubbelohde²³².

Formic acid, acetic acid, propionic acid, butyric acid, diethyl peroxide, ethyl hydrogen peroxide, ether, butyraldehyde, acrolein, crotonaldehyde, glyoxal, diacetyl, furfuraldehyde, furyl alcohol, furoic acid, furan, methyl furan, tetrahydromethylfuran, tetrahydrofuryl methyl ether, α angelilactone, β angelilactone, dihydropyran, tetrahydropyran, dimethyl keten, acetyl acetone, ethyl acetoacetate, amylene, ethylene, phenol, naphthalene, methyl iodide.

IV. THE SPECTRA OF VARIOUS ORGANIC FLAMES

Outer Cones.

The outer cones of all ordinary organic flames show chiefly the OH bands and the carbon monoxide flame spectrum. In some cases the CH bands appear weakly in the outer cone, and if the inner cone of the flame is chilled, then the hydrocarbon flame bands are also present in the outer cone. The bands of NO and the spectra of various metallic oxides may also spread into the outer cones of flames when the appropriate metals are present.

Inner Cones.

In the following table the strength of the principal band systems occurring in the inner cones of compounds containing carbon, hydrogen, oxygen, nitrogen and the halogens are given. The numbers 1, 2, 3, and 4 indicate that the system is very weak, weak, moderate, or strong, respectively. The table is largely based on the observations published by Vaidya ^{237 240}, Guénault ¹⁰⁶, Smith ²¹⁹, Bell ¹⁶ and the author. The hydrocarbon (or ethylene) flame bands are listed under HCO for convenience.

Fuel	OH	CH	C,	HCO	Other features
CH ₄ Methane . . .	4	3	3	2	
CCl ₄ +H ₂ Carbon tetra- chloride . . .	4	4	4	2	CCl.
CH ₂ O Formaldehyde . . .	4	—	—	—	CO flame.
CHOOH Formic acid . . .	3	—	—	—	CO flame.
CH ₃ OH Methyl alcohol . . .	4	2	?1	?	Cool flame of ether.*
CHCl ₃ +H ₂ Chloroform . . .	4	4	4	2	CCl.
CH ₂ Cl Methyl chloride . . .	4	4	4	2	CCl, trace CN.
CH ₃ I Methyl iodide . . .	?4	?4	?4	?2	IO.
C ₂ N ₂ Cyanogen . . .	—	—	?4	—	Strong CN. NH if moist.

* Guénault reported, and confirmed in a later paper, the presence of the cool flame spectrum of ether (formaldehyde) in the flame of methyl alcohol. Bell reported the presence of the hydrocarbon flame bands. Vaidya observed neither of these systems in the ordinary flame, but found the cool flame bands of ether in the atomic flame of methyl alcohol.

Fuel	OH	CH	C ₂	HCO	Other features
C ₂ H ₂ Acetylene . .	3	4	4	3	Little CN, NH and NO.
C ₂ H ₄ Ethylene . .	3	4	4	4	
C ₂ H ₆ Ethane . .	4	3	3	2	
CH ₃ CHO. Acetaldehyde	4	4	3	2	
C ₂ H ₅ Br Methyl bromide	14	14	14	12	BrO.
C ₄ H ₁₀ Butane . .	4	4	3	2	Trace CN and NH.
C ₂ H ₅ OC ₂ H ₅ Ether . .	4	4	4	3	
C ₅ H ₅ N Pyridine . .	3	3	3	2	Strong CN and some NO.
C ₆ H ₆ Benzene . .	3	4	4	3	
C ₆ H ₅ OH Phenol . .	4	4	4	3	
C ₆ H ₄ (OH) ₂ Resorcinol .	3	3	3	2	
C ₆ H ₃ (OH) ₃ Pyrogallol .	3	3	3	2	
C ₆ H ₅ NO ₂ Nitrobenzene	3	3	3	1	Strong CN and some NO.
C ₆ H ₅ NH ₂ Aniline . .	3	3	3	1	Strong CN and some NO.
C ₆ H ₅ CH ₃ Toluene. . .	4	4	4	3	
C ₆ H ₅ CHO Benzaldehyde	3	3	3	2	
C ₆ H ₅ COOH Benzoic acid	3	3	3	2	
C ₆ H ₅ OC ₆ H ₅ Diphenyl oxide	3	3	3	3	

Atomic Flames.

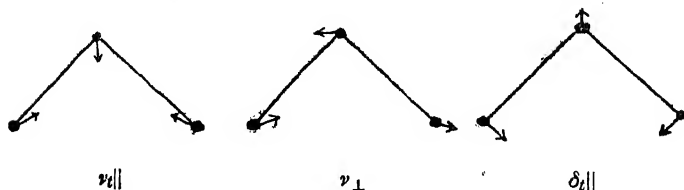
Based on observations by Geib and Vaidya ⁹⁵.

Flame	OH	CH	C ₂	HCO	Other features
H + C ₆ H ₆ Benzene . .	—	4	4	—	
O + CH ₂ O Formaldehyde	4	—	—	—	
O + CH ₃ OH Methyl al- cohol	4	1	?	—	Cool flame of ether.
O + C ₂ H ₂ Acetylene . .	3	4	4	3	Little CO flame.
O + C ₂ H ₄ Ethylene . .	4	3	2	1	
O + C ₆ H ₆ Benzene. . .	4	4	4	3	Little CO flame.

V. SOME ATOMIC AND MOLECULAR ENERGY LEVELS AND MOLECULAR CONSTANTS

In this table brief data for the low energy states of carbon, hydrogen, oxygen, nitrogen and simple compounds of these elements are collected. The values given are based on those collected by Bacher and Goudsmit ⁵, Sponer ²²¹, Herzberg ¹²³ and King ¹⁴²; some of the data for NH are from the paper by Lunt, Pearse and Smith ¹⁷⁰, and for O₃ by Sutherland and Penney ²²⁴. All values are expressed in cm.⁻¹ except dissociation energies which have been converted to k.cal./mol. Uncertain values are bracketed. In some cases where data for ω_e and B_e are not available, values of ω_x and B_o respectively are given, these being printed in italics for distinction. Values of ω_e which are derived from measurements of band heads instead of band origins are indicated by the letter H following the value.

The three fundamental vibrational frequencies for triangular molecules are denoted by $\nu_{||}$, ν_{\perp} and $\delta_e||$ as follows:



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	State	Energy above ground- state	ω_e	$x_e\omega_e$	B_e	Disso- ciation energy (k.cal.)	Dissociation products
C	3P_0	0					
	3P_1	14.8					
	3P_2	42					
	1D_2	10,192					
	1S_0	21,647					
	5S	(34,994)*					
	V	(56,000)†					
C ₂	$^3\Pi_u$	0	1641.7	11.7	1.632	87	C(3P)+C(3P)
	$^1\Sigma^+$?					
	$^1\Pi_u$?	1608.3	12.1	1.617		
	$^3\Pi_g$	19,379	1792.5	19.3	1.758		C(3P)+C(1D)
CH	X $^2\Pi$	{ 0 28.5	2824	46	14.453	80.0	C(3P)+H(2S)
	A $^2\Delta$	23,163	(2800)		14.5		?C(1D)+H(2S)
	B $^2\Sigma^-$	25,715	(2242)		12.62		?C(3P)+H(2S)
	C $^2\Sigma^+$	31,810	(2906)	(102)	14.62		?C(1D)+H(2S)
CN	X $^2\Sigma^+$	0	2068.7	13.1	1.899	147‡	C(3P)+N(4S)
	A $^2\Pi$	{ 10,877 10,929	1788.7	12.9	1.699		C(3P)+N(4S)
	B $^2\Sigma^+$	25,798	2164.1	20.2	1.970		C(3P)+N(2D)
CO	X $^1\Sigma^+$	0	2168.2	13.0	1.931	256‡	C(3P)+O(3P)
	a $^3\Pi$	48,438	1739.3 _H	14.5	1.686		C(3P)+O(3P)
CO ₂	$^1\Sigma_g^+$	0	ν_1 (1336)§ ν_2 667.5 ν_3 2350.1			(264)	?O(3P) +CO($a^3\Pi$)
H	$^2S_{1/2}$	0					
H ₂	$^1\Sigma_g^+$	0	4405.3	125.3	60.87	103.2	H(2S)+H(2S)
H ₂ O		0	$\nu_{d }$ 3600 ν_{\perp} 3756.3 $\delta_{d }$ 1595.4			218.9	H(2S)+O(3P) +H(2S)
N	$^4S_{1/2}$	0					
	2D	19,202					
N ₂	X $^1\Sigma_g^+$	0	2359.6 _H	14.4	2.007	170.1	N(4S)+N(4S)
	A $^3\Sigma_u^-$	49,774	1460.4 _H	13.9	1.440		N(4S)+N(2D)
NH	X $^3\Sigma^-$	0	(3300)		16.33	(78)	N(4S)+H(2S)
	a $^1\Delta$?	3060		16.46		N(2D)+H(2S)
	b $^1\Sigma^+$?			16.40		N(3P)+H(2S)
	A $^3\Pi$	29,780	(3300)		16.29		N(2D)+H(2S)
	c $^1\Pi$?	2270		14.16		N(2D)+H(2S)
NO	X $^2\Pi$	{ 0 120.9	1906.5	14.5	1.709	122	N(4S)+O(3P)
	A $^2\Sigma^+$	44,199	2374.3	16.3	2.00		
	B $^2\Pi$	{ 45,486 45,514	1036.9 1038.2	7.5 7.5	1.076 1.177		
NO ₂		0	$\nu_{d }$ 1370 ν_{\perp} 1615 $\delta_{d }$ 640			77¶	NO($^2\Pi$)+O(3P)
O	3P_2	0					
	3P_1	158.1					
	3P_0	226.8					
	1D_2	15,867.8					
	1S_0	33,792.8					

	State	Energy above ground state	ω_s	$x_s \omega_s$	B_s	Disso- ciation energy	Dissociation products
O_2	$X^3\Sigma^-$	0	1580.4	12.1	1.446	117.2	$O(^3P) + O(^3P)$
	$a^1\Delta_g$	7,881.6	(1500)		1.415		$O(^3P) + O(^3P)$
	$A^1\Sigma^+$	13,121	1432.6H	13.9	1.401		$O(^3P) + O(^3P)$
	$C^3\Sigma^+$	(38,000)			0.84		$O(^3P) + O(^3P)$
	$B^3\Sigma_u^-$	49,358	709.6	10.7	0.820		$O(^3P) + O(^1D)$
O_3		0	$\nu_2 1037$ $\nu_1 1740$ $\delta_t 710$			30¶	$O_2(^3\Sigma_g^-) + O(^3P)$
OH	$^2\Pi$	$\begin{cases} 0 \\ 139.1 \end{cases}$	3727.9	78.1	18.862	99	$O(^3P) + H(^3S)$
	$^2\Sigma^+$	32,465	3184.1	97.7	17.383		$?O(^1D) + H(^3S)$

* Value calculated by Bacher and Goudsmit *.

† Van Vleck's valence state, see page 146.

‡ See pages 142-144.

§ CO_2 is a linear symmetrical molecule. ν_1 is the symmetrical valence vibration, ν_2 is the transverse vibration, and ν_3 the antisymmetrical valence vibration. The near equality $\nu_1 = 2\nu_3$ results in a degeneracy, the combined levels giving rise to two at 1285.8 and 1388.4 cm^{-1} .

¶ See page 145.

VI. PHYSICAL CONSTANTS, ETC.

c	velocity of light, 2.9978×10^{10} cm./sec.
e	electronic charge, 4.80×10^{-10} e.s.u.
h	Planck's constant, 6.62×10^{-27} erg/sec.
k	Boltzmann factor, 1.381×10^{-16} erg/deg.
N	Avogadro's number, 6.02×10^{23} mols./gm.mol.
n	Loschmidt's number, 2.685×10^{19} mols./c.c. at N.T.P.
m_e	mass of electron, 9.1×10^{-28} gm.
m_H	mass of hydrogen atom, 1.66×10^{-24} gm.
1 Å. (angstrom)	= 10^{-8} cm.
1 μ (micron)	= 10^{-4} cm.
1 gm. calorie	= 4.185×10^7 ergs.
1 electron-volt	= 1.60×10^{-12} ergs.
1 electron-volt	= 8066 cm. ⁻¹ (wave-numbers).
1 electron-volt	= 23,053 gm. calories/mol.
1 cm. ⁻¹	= 2.86 gm. calories/mol.
k.T at 1° K.	= $0.697 \text{ cm.}^{-1} = 1.99 \text{ gm.cal./mol.} = 8.53 \times 10^{-5} \text{ e.v.}$

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Note.—Radicals are indexed under their chemical symbols (e.g. OH and CH_2 rather than hydroxyl and methylene radical), while chemically stable substances are indexed under their usual names (e.g. oxygen, hydrogen sulphide and benzene rather than O_2 , H_2S and C_6H_6).

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